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CONFERENCE ON THE

Vibrational Spectra of High Polymers

Held under the auspices of the
Centro Nazionale di Chimica delle Macromolecole
Consiglio Nazionale delle Ricerche
Istituto di Chimica Industriale del Politecnico
Milano, Italy, July 18-20, 1963

edited by *Giulio Natta* and *Giuseppe Zerbi*

Consiglio Nazionale delle Ricerche
Istituto di Chimica Industriale del Politecnico, Milano

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Introduction

In this volume are collected the invited and contributed papers delivered at the Conference on Vibrational Spectra of High Polymers held at Milano during July 18–20, 1963. The Conference was organized under the Sponsorship of the Chemistry Committee of the National Research Council of Italy through its National Center for the Chemistry of Macromolecules.

The Conference was arranged by a Scientific and Organizing Committee under the direction of Prof. Giulio Natta and Prof. G. B. Bonino.

Chairman of the Conference was Prof. G. B. Bonino.

After the meeting the speakers submitted the texts of their papers. Following each paper is a discussion. The text of the discussion is based on a tape-recording of the actual discussion, the transcript of which was then abridged and revised, and corrected by the participants.

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SURVEY PAPERS

JOURNAL OF POLYMER SCIENCE: PART C NO. 7, PP. 3–18

Recent Developments in the Vibrational Spectroscopy of High Polymers

S. KRIMM, *Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan*

Introduction

The holding of a conference devoted to the vibrational spectroscopy of high polymers attests to the importance which this technique is assuming in the study of macromolecules. The rapidity of this development can be judged from the fact that a review of the detailed spectral assignments of polymers which appeared in 1960[1] could already use revision of some assignments for almost every polymer discussed. The reasons for this rapid progress are easy to trace. They have their roots in the realization that not only is it desirable but indeed it is possible to treat macromolecules with the same depth of analysis formerly reserved for small molecules. This conference takes place most happily amidst the flowering of these studies.

To see the recent developments in proper perspective it may be useful to remind ourselves very briefly of the relevant historical background of polymer spectroscopy. Early studies of the spectra of high polymers (see, for example, reference 2) depended largely on the use of group correlations to obtain information on chemical structure. Such correlations have since been developed in great detail,[3] and often have important analytical uses. Although the study of some of these diagnostic bands by means of techniques such as dichroism was able to provide significant information on physical structure,[4,5] the potentialities of vibrational spectroscopy in the study of macromolecular structure were yet to be fully realized. A step forward was made soon after (see for example references 6 and 7) when the normal modes of a simple known polymer structure, polyethylene, were calculated. This was an important forerunner of the more detailed calculations now being done. In the mid-1950's a new point of view emerged in the study of polymer spectra, viz., the attempt to achieve a complete interpretation of the spectrum. It was felt that only in this way could the full power of spectroscopy as a tool in the study of polymer structure and properties be achieved. Symmetry analysis[8,9] as well as a variety of experimental techniques were used as part of this expanded investigation, and a number of polymers were studied in this way.[10–13] The results of this and subsequent work along these lines were discussed in the above-mentioned review.[1]

The present developments in polymer spectroscopy stem from this concentration on the detailed assignment of bands in the spectrum. Progress is being made in several directions, of which, perhaps two major ones stand out at the present time. First, a significant improvement has occurred in the treatment of normal vibrations of helical polymer molecules, and since the early 1960's we have seen increasing application of this very important cornerstone of spectral analysis.[14–17] Other contributors to this conference will report in greater detail on the results of these studies, so no further comment will be undertaken here. Suffice it to say that as a result of these studies the analysis of the crystalline component of polymers is on a firm foundation. Second, techniques are developing which permit the identification and assignment of bands associated with the non-crystalline component of polymers, a component which is neither negligible in its physical importance nor in its spectral contribution. The study of spectral differences which arise from the presence of non-crystalline structures and the identification of such structures will be the main concern of the present remarks.

Spectra of Non-Crystalline Components of Polymers

It is of course a well-known fact that a certain portion of the chains in a polymer specimen exist in non-crystalline structures. The latter contribute to the amorphous type of scattering found in the x-ray diffraction pattern of most polymers, and in general give rise to infrared bands different from those of the chains in the crystalline regions. Before considering the origin of such spectral differences it is worthwhile noting the experimental consequences of this simultaneous presence of different kinds of chain structures.

Absorption bands of polymers are usually quite broad, having half-widths occasionally less than 10 cm.$^{-1}$ but usually in the range of 10 to 20 cm.$^{-1}$. This has perhaps given rise to a prevalent view that spectral resolution is not of great importance for the study of polymers. The presence of several chain structures, however, with small frequency differences between them, might already indicate the need for resolving closely spaced bands, and recent evidence (which we will mention later) demonstrates that this is in fact the case. It is therefore of great importance that a strong effort be made to achieve high spectral resolution in order to resolve such overlapping. Only in this way will it be possible to identify the bands which are associated with the different chain structures.

There are several methods by which such resolution can be achieved for polymer spectra. First, and most obvious, is to use spectrometers of higher resolving power. As we shall see, grating spectrometers provide usefully better resolution than prism instruments in studying high polymers. Second, a variation of crystallinity in a specimen can in effect lead to the "resolution" of adjacent bands. Thus, if an observed band is an unresolved composite of a crystalline and a non-crystalline component, then by varying the degree of crystallinity the change in band shape and/or maximum will be a clue to the presence of more than one component. Such

variation in crystallinity can be achieved by, for example, changing the temperature of the specimen or by changes in polymerization conditions which lead to polymers of different crystallinity. Third, dichroic measurements on oriented polymer specimens often permit the identification of closely adjacent bands. This is the case when a composite band contains components of different dichroism: the band maxima of each component will appear at different frequencies in radiation of the appropriate polarization. Fourth, the spectra of deuterated polymers often reveal band overlaps. This is obviously the case when one component is a hydrogen frequency, since it is shifted by a large amount on deuteration. But it is also true of non-hydrogen frequencies; because of their differential mixing with hydrogen and skeletal modes, adjacent bands arising from similar types of vibrations in different structures can be affected differently by deuteration. The last three methods were of particular importance in the resolution of bands in the spectrum of polyvinyl chloride.[18]

Turning now to the origins of spectral differences between crystalline and non-crystalline polymers, we should note that a polymer chain crystallizes because chain order of some kind is possible. For stereoregular polymers this order includes both main chain as well as side chain atoms, so that in isotactic polypropylene for example, true helical symmetry exists in the crystalline regions. In some cases it appears to be possible to have ordered skeletal structures with varying degrees of order in the side chain atoms. Thus nontactic polyvinyl alcohol seems to crystallize with a planar zig-zag carbon skeleton although there is no regularity in the placement of the pendant OH groups.[19] Similarly, in poly-3,3-bis(chloromethyl)oxacyclobutane, $+CH_2C\ (CH_2Cl)_2\ CH_2O+_n$, (PCOB) it appears that two different crystal structures occur in which the main chain structures are the same but different side chain isomeric structures are possible.[20] From the spectral point of view, however, the structure of the polymer chain in the crystal is usually well-defined, and it is pertinent to inquire into the factors which can give rise to spectra which are different from that for this crystalline structure.

When a stereoregular polymer chain is removed, without change in conformation, from its crystalline environment we may in general expect small shifts in frequency for some of its normal vibrations. This is a reflection of the static field effect, i.e., the contribution of the arrangement of neighboring molecules to the potential at the site of the molecule in question. An effect of this kind seems to be operative in the *n*-paraffins and polyethylene. Thus, it is found[21] that for a solid solution of an *n*-paraffin in a deuteroparaffin the CH_2 rocking mode occurs at 725 cm.$^{-1}$ (the solid solution causes the intermolecular interaction splitting to disappear) whereas at the melting point of the *n*-paraffin this band is found at 720 cm.$^{-1}$. There is still a significant amount of planar zig-zag chain in the melt, so we are led to conclude that the 5 cm.$^{-1}$ shift arises primarily from the differing environments in the crystal and in the liquid. In fact, in the triclinic form of the crystal, where there is only a single band, this mode occurs at 715

cm.$^{-1}$,[22] again reflecting the alteration in the field at the site of the molecule due to the different equilibrium arrangement of neighbors. Therefore, it can be expected that polymer chains present in non-crystalline regions but having the same conformation as those in the crystalline regions will have slightly different frequencies associated with their normal vibrations.

In the above discussion we have assumed that the chain in the non-crystalline region preserves its conformation, usually helical, over distances comparable to that in the crystal. This will usually not be the case, since the less ordered structure of the non-crystalline regions generally requires that bends occur in the chain. Such bends in the chain, which are generally a result of rotation about C—C bonds, provide several bases for spectral changes. The change from an essentially infinite chain to a short segment might have an effect due to symmetry alterations alone. Thus, whereas non-factor group fundamentals are prohibited for the infinite chain such modes can exhibit activity in a finite chain.[23] This means that activity can be permitted to modes in which the phase of vibration in adjacent units is other than the few specific values allowed in the infinite helical chain. Again, the reduction from the infinite chain symmetry may result in the relaxation of factor group selection rules such that previously forbidden modes can become allowed. When this decrease in symmetry occurs within the chain unit the appearance of previously forbidden bands may be most pronounced. This seems to be the case for polyethylene terephthalate,[24,1] where some bands associated with the non-crystalline regions are assignable to Raman-active infrared-inactive modes of the *p*-disubstituted benzene ring. These have presumably become activated in the infrared spectrum by the loss of a center of symmetry in the non-crystalline chains.

In addition to such spectral effects arising from the symmetry changes associated with shortening of helical segments, we may also expect direct influences on the normal vibrations. This will be likely to occur via alterations in the interactions between neighboring units, for example as a result of end effects, and could well influence different modes to different extents. There has not been sufficient theoretical study of the dependence of normal vibrations upon helix length, but some of the expected effects may be inferred from recent experimental work. Thus we know that interactions between similar vibrations in neighboring units of an infinite helix lead to a difference in frequency between the A modes and the E modes of vibration.[25] This interaction splitting can be a function of helix length, and results for polystyrene[26] and polyoxymethylene[14] suggest that this is in fact the case: the splitting of such π,σ pairs of bands increases as the specimen crystallinity is increased. In the case of polystyrene it is also found[26] that a σ,σ doublet has a frequency splitting which is a similar function of helix length. While not completely understood, this effect also seems to be correlated with the variation in intrachain interaction with the length of repeating structure. An important consequence of this variation in interaction with helix length is that it may affect different modes to different extents. Thus, essentially side chain vibrations which interact little with the main

chain vibrations may be sensitive to the local conformation but not to the longer range helical order. On the other hand, when there is significant mixing with main chain skeletal modes, the influence of long range order can be important. This may be the origin, for example, of the behavior of the 975, 998 cm.$^{-1}$ pair of bands in polypropylene with changes in crystallinity and tacticity. These bands are due to CH_3 rocking modes admixed with varying amounts of skeletal CC stretching.[16] Therefore, the disappearance of the 998 cm.$^{-1}$ band when isotactic polypropylene is melted[27] may indicate that long range helical order is necessary for the existence of the associated vibration, whereas the disappearance also of the 975 cm.$^{-1}$ band in an atactic polymer[28,29] may show that even the short range helical order required for the presence of this band is absent.

So far we have been concerned with the spectra of the helical portions of chains. As indicated, in the non-crystalline "regions" helical chain segments are separated from other such segments by bends. It is necessary now to consider the spectral contribution of these bends. A departure from helical symmetry occurs usually by rotations around C—C bonds. Because of the hindered rotation barrier around such a bond only the positions close to the staggered ones are permitted to the groups attached to the two carbon atoms. If rotations around one or more bonds are meaningful then several different rotationally isomeric structures are possible at the bends. In general these have different spectra,[30] and in some cases these spectra have been used to identify the rotationally isomeric structures involved.[18] Thus, we can expect a spectral contribution which is associated with new structures derived by rotations around C—C bonds.

Finally, we must consider the contribution of chains having relatively atactic sections. These sections are in general most likely to be found in the non-crystalline regions, and they may exhibit a range of structures. We have reason to believe, however, that the number of structures is small (some perhaps being most favored energetically), and most important, that the possible conformations are determined by the local configuration of the chain. Usually it is possible to surmise what these conformational structures are, and if they can be identified in the spectrum then the configurational structure can be determined. Particular local conformations are often different in detail (say at the next nearest neighbor position) when they arise from tactic or atactic structures, so a detailed analysis of the spectrum may permit information to be obtained on the stereoregularity of the polymer.

We see, therefore, that there are many ways in which spectral contributions can arise other than from the clearly defined structure of the polymer chain in the crystalline regions. In order to define fully the structure of a polymer specimen we must be able to identify the exact origin of these non-crystalline contributions to the spectrum. Unfortunately, not much theoretical work has been done along these lines, an area in which more study is greatly needed. In some cases experimental studies have permitted a deeper insight into these phenomena and therefore allowed a de-

tailed analysis of the spectra to be achieved. We will be concerned in the remainder of this paper with one of the sources of spectral alteration discussed above, viz., rotational isomerism, and its application to the study of non-crystalline polymer structure.

Study of Isomeric Structures in Polyvinyl Chloride

Polyvinyl chloride (PVC) has been a particularly favorable system in which to demonstrate the existence and carry through the analysis of isomeric structures resulting from rotations about C—C bonds in the chain. We will therefore review this case carefully.

Early x-ray results[31] led to the suggestion that the main component of PVC is a syndiotactic chain structure, and this has been confirmed by more recent x-ray work[32] and by infrared studies.[15,18] Nevertheless, a high degree of stereoregularity is found only in polymers synthesized under special conditions; the ordinary polymer contains a significant fraction of material which is not syndiotactic. The effect of this component on the spectrum is shown in Figure 1.[33] Here we see the C—Cl stretching region of the spectrum for polymers obtained by polymerization under different conditions. That polymerized in a urea complex, and known to be the most crystalline, shows only two bands, at 602 and 640 cm.$^{-1}$ This is what would be expected for the syndiotactic structure,[12,18] and it is consistent with the results of normal vibration calculations.[15] The effect of polymerization under other conditions is seen to be the introduction of absorp-

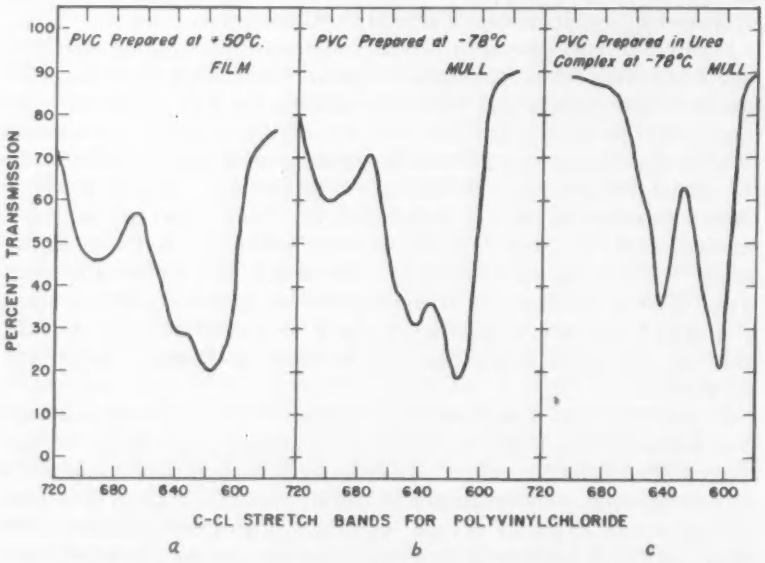

Fig. 1. Infrared spectra of different polyvinyl chloride polymers in the C—Cl stretching region.[33]

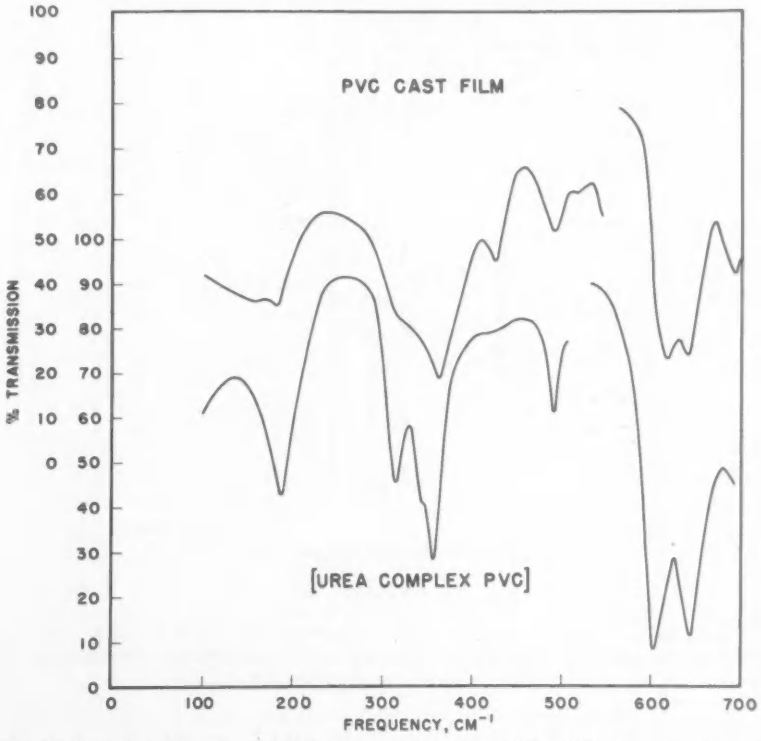

Fig. 2. Far infrared spectra of PVC polymers: cast film of +50°C. polymer, and urea complex polymer.[34]

tion near 615 cm.$^{-1}$ and 690 cm.$^{-1}$, and it may be inferred that structures other than the planar zig-zag syndiotactic chain are therefore present. The problem is to identify these. It might be noted incidentally that such differences are observable throughout the spectrum, and in particular in the far infrared region, as shown in Figure 2.[34] The far infrared region of the spectra of polymers has not been investigated in as great detail as the other regions but it may well be of major importance in the study of conformational structure.

The clues to the unraveling of the complex band structure in the C—Cl stretching region of the spectrum came from two main results. First was the detailed identification of the major non-crystalline bands in this region. This was accomplished in part by studies on partially deuterated polymers,[18] as a result of which a new band was revealed at 638 cm.$^{-1}$ (normally overlapped by the 640 cm.$^{-1}$ crystalline band). In addition studies with a grating spectrometer giving higher resolution[35] revealed another band, as shown in Figure 3: whereas previously one strong band was observed near 615 cm.$^{-1}$ (see Fig. 1) it is now seen that this band consists of a strong

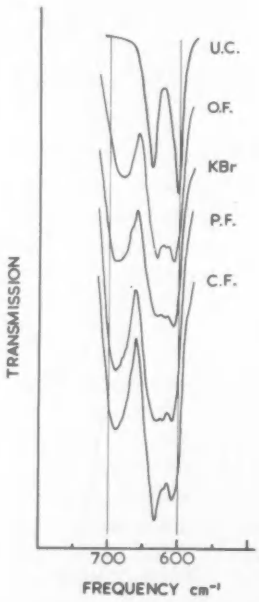

Fig. 3. Infrared spectra of +50°C. PVC polymer in various physical states. O.F. = oriented film, KBr = KBr pellet, P.F. = pressed film, C.F. = cast film. The spectrum of a urea-complex polymer (U.C.) is shown for comparison.[35]

component at 610 cm.$^{-1}$ and a weak one at 620 cm.$^{-1}$. The second observation of importance was that the frequency region in which the C—Cl stretching vibration is located is a very sensitive function of the local conformation.[30] In particular, studies on model compounds showed that this frequency is correlated with the two substituents trans to the secondary Cl atom across both neighboring C—C bonds (see Table I). Designating these substituents as hydrogen (H) or carbon (C), the frequency ranges for the secondary (S) chlorine vibrations were found to be: S_{HH}: 608–615 cm.$^{-1}$, S'_{HH}: 627–637 cm.$^{-1}$, S_{HC}: 655–674 cm.$^{-1}$. In this designation S_{HH} indicates a planar zig-zag carbon chain at least five atoms long (chlorine located on carbon atom 3) while S'_{HH} is a structure formed when a chain bend occurs at carbon atom 4 (or 2) but in such a way that the Cl atom still has H atoms trans on both sides. The existence of the latter structure has been verified by electron diffraction studies on 2-chlorobutane,[36] and it is found that this structure is associated with a characteristic infrared band.[30]

Assignments of the non-crystalline bands of PVC to isomeric structures can now be made on the basis of the above correlations from model compounds. These are shown in the first two columns of Table II. In making these assignments we need to assume a slight shift in the centers of the fre-

TABLE I
Carbon—Chlorine Stretching Frequencies for Secondary Chlorides

Structure	S_{CC}[a] (cm.$^{-1}$)	S_{HC}[a] (cm.$^{-1}$)	S'_{HH}[a] (cm.$^{-1}$)	S_{HH}[a] (cm.$^{-1}$)
1. $CH_3-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_3$		No band	No band	611 s
2. $(CH_3)_3-C-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_3$		667 s	No band	No band
3. $(CH_3)_3-C-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-C-(CH_3)_3$	785 s	No band	No band	No band
4. $CH_3-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_2-CH_3$		671 m	628 m	609 s
5. $CH_3-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-(CH_2)_2-CH_3$		670 m	No band	612 s
6. $CH_3-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-(CH_2)_3-CH_3$		670 m	No band	611 s
7. $CH_3-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-(CH_2)_5-CH_3$		672 m	No band	611 s
8. $CH_3-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_2-CH(CH_3)_2$		674	No band	615 s
9. $CH_3-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_2-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_3$		678 m	627 sh	609 s
10. $CH_3-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-CH_2-CH_3$	749 m	667 m 655 m	628 sh	609 s
11. $CH_3-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-(CH_2)_2-CH_3$	753 m[b]	663 m	637 w	608 s
12. $CH_3-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-(CH_2)_3-CH_3$	733 m[b]	661 m	635 w	608 m
13. $CH_3-(CH_2)_2-\underset{\displaystyle Cl}{\underset{\vert}{CH}}-(CH_2)_3-CH_3$	733 m[b]	662 m	635 w	610 m

[a] s = strong; m = medium intense; w = weak; sh = shoulder.
[b] May be confused with CH_2 rock.

quency regions for particular isomeric structures in the polymer as compared to those of the model compounds. This might be due to different effects of neighboring molecules in the two cases, or to small differences in the hindered rotation angle for the small as compared to the large molecules. The assignment of the newly observed 620 cm.$^{-1}$ band to an S_{HH} mode is consistent with these correlations. The assignment of the 638 cm.$^{-1}$ band to an S'_{HH} mode is also strongly indicated.[18] We cannot assign this band to an S_{HH} mode by analogy with a similar assignment for the 640 cm.$^{-1}$ band, because the latter is part of a split doublet (the other component being at 602 cm.$^{-1}$), the mean value of the pair falling in the range of the

TABLE II
ν(CCl) Frequencies of Polyvinyl Chloride

Frequency	Isomeric structure	Chain conformation	
602	S_{HH}	(TT)TT(TT)	$s(B_1)$
610	S_{HH}	...TT...	s
620	S_{HH}	(TG)TT(G*T)	i
638	S'_{HH}	(TG)(TG*)(TG)	i
640	S_{HH}	(TT)TT(TT)	$s(A_1)$
685	S_{HC}	(TG)TG(TG)	i
693	S_{HC}	(TT)GG(TT)	s

S_{HH} frequency. (It is interesting to note that both theory[15] and experiment[37] indicate that the interaction splitting gives rise to components about equally shifted from the unperturbed frequency.) There is also no evidence that the 638 cm.$^{-1}$ band is correlated with any other band at lower frequencies. In fact, the opposite is true: in solutions of PVC the 638 cm.$^{-1}$ band is almost absent, but that centered at 615 cm.$^{-1}$ is still strong.[38,39]

It is now possible to associate these isomeric structures with specific chain conformations. These in turn can be derived from particular chain configurations expressed in terms of syndiotactic (s) and isotactic (i) pair placements. This is shown in columns three and four of Table II. The conformations can be deduced with the help of molecular models,[18,39] or on the basis of energy considerations.[40–42] The choice in assigning the 620 cm.$^{-1}$ band to the isotactic structure and the 610 cm.$^{-1}$ band to the syndiotactic structure is based on the relative band intensities and on the expected fewer number of ways in which the former structure can be realized as compared to the latter. The assignment of the 685 and 693 cm.$^{-1}$ S_{HC} modes to the i and s configurations respectively is based on the dichroism of these two bands, σ and π, which is what would be expected for these structures.[18] The 638 cm.$^{-1}$ band contains contributions from higher energy structures, the main one probably being that shown in Table II and corresponding to a small displacement in an isotactic helix. Such structures undoubtedly exist as a result of the contraints imposed on the chains in the solid state, and it is not unexpected that these constraints diminish in solution (as noted).

With the sensitivity to conformation available in these C—Cl stretching frequencies it has been possible to show that the conformational structure of a PVC specimen is a function of its physical state.[39] This is also seen in Figure 3, in which the spectra of a KBr disk, a pressed film, and a cast film of unoriented PVC show in particular the change in relative intensity of the 638 cm.$^{-1}$ band with treatment. Similar changes occur for an oriented film. That such intensity changes are not due primarily to the effects of the orientation in this case is indicated by the shift in maximum from 693 to 685 cm.$^{-1}$. Since the former is a π band and the latter is σ, orientation alone would favor the intensity of the former band. That the opposite occurs is an indication that the proportion of isomeric structures is altered

by stretching. It is interesting to note that in this case the changes indicated in the spectrum seem to be in agreement with the expected physical processes taking place. The 693 cm.$^{-1}$ band is assignable to the syndiotactic S_{HC} structure (see Table II), and its decrease in relative intensity upon elongation is therefore to be interpreted as a diminution in the proportion of such structures. There are at least two ways in which this is likely to occur.[30] First, elongation of the specimen should be accompanied by conversion of less extended into more extended chain conformations. The S_{HC} structures of syndiotactic regions correspond to the former, and their disappearance is consistent with the conversion of S_{HC} conformations to the S_{HH} conformations of the more extended planar zig-zag chains. Second, if the crystalline syndiotactic regions are made up of folded chain crystals, it is likely that the folds contain S_{HC} structures. If the external stress causes the chains to unfold and reorient in the stretching direction, then a decrease in the number of S_{HC} structures is to be expected. Thus, knowledge of the correlations of spectral bands with noncrystalline chain structures permits interpretation of conformational changes associated with physical processes.

Conclusion

We have seen that rotationally isomeric structures give rise, as expected, to significant new absorption bands in the infrared spectra of polymers. These, as the results on PVC suggest, can be interpreted in terms of specific chain conformations, which in turn are often derivable from particular configurations.

At present the indication is that molecules containing chlorine (and presumably other halogen) atoms will be particularly favorable for permitting detailed assignments of rotationally isomeric structures. This has proved to be true also for the PCOB molecule referred to earlier.[20] In this case not only are the carbon-chlorine stretching frequencies sensitive to different side chain conformations, but CH_2 bending and wagging modes also display this dependence. The latter modes are in fact so well separated in frequency that their dichroism and temperature behavior can be used to identify the isomeric structures present. However, in addition to halogen-containing molecules we must expect such isomeric structures in other types of polymers as well, and must seek comparable methods for analyzing for their presence. Normal vibration calculations on model structures analogous to these chain conformations will undoubtedly be of great importance in identifying them with certainty.

In this paper we have dealt with only one of the factors giving rise to non-crystalline spectral bands, viz., rotational isomerism. It is clear that the other factors mentioned earlier may also be contributing to spectral differences. If we hope to use the vibrational spectrum to study polymer structure, then we must be prepared to extend the analysis in as much detail to the non-crystalline structures as has already been done for the crystalline

structures. The overwhelming success which has been achieved for the latter should give us the courage to tackle the former.

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Discussion

P. Corradini (*Universita di Napoli, Italy*): Could the 638 cm.$^{-1}$ band represent a conformation other than S'_{HH}, its frequency having been shifted by the effect of different neighboring structures?

S. Krimm: Let me answer the question in the following way: you may remember that I said that both the syndiotactic as well as the isotactic regions should give rise to what we call S_{HC} frequencies. If everything were as simple as indicated you might at first say that such frequencies should be the same because the correlations that we are getting from small molecules are only local correlations of structure. We are not seeing anything further beyond, let us say, the conformation about the two immediate C—C bonds. In fact, the frequencies are not identical in polyvinyl chloride. The isotactic band is at 685 cm.$^{-1}$ and the syndiotactic one is at 693 cm.$^{-1}$ There is a small shift of about 8 cm.$^{-1}$. Now, if you make a model of the syndiotactic and the isotactic molecule, right around the carbon chlorine bond you see immediately a H *trans* to Cl and a C *trans* to this Cl. As you go to the next carbon atom there are slight differences in the skeletal framework; they are not identical even for these two. That means that there must presumably be second order effects. Now we get back to S'_{HH}. The question is: if we examined a situation where there were two chlorine atoms, would we see this band in a significantly different range than we do for one chlorine atom? I think that the range roughly in which we see S'_{HH}, while it may shift slightly, will not shift drastically. For example in the model compounds, this frequency occurs in the range 627 to 637 cm.$^{-1}$. I think that there is a possibility that this range may shift slightly as a result of next neighbor effects, but I still think the prime influence is what is trans on either side of the carbon chlorine bond. Now if one simply looks at the way in which these regions in the model compound compare with the regions in the polymer, it seems that a very good correlation can be made with hardly more than perhaps a 5 cm.$^{-1}$ shift of the centre of the region. The only other possibility would be to correlate the 638 cm.$^{-1}$ band either with S_{HH}, or with S_{HC} up around 670–680 cm.$^{-1}$. S_{HH} is down in the region of about 610–620 cm.$^{-1}$ My own feeling is that the 638 cm.$^{-1}$ band is a little too far away to fit into either of the two; but it does fit in with the band found for 2-chlorobutane which falls right around this position. I am not saying that the structure in the polymer is identical in terms of the angle of rotation to what it is in 2-chlorobutane. Maybe the contacts in the polymer cannot be the same as in 2-chlorobutane because of the structure, and therefore perhaps there has to be a rotation of several degrees away from the equilibrium position. But I think that the general structure must be similar to the one that we surmised from the 2-chlorobutane case. I think this is an important point and I ought to say why. As I understand it, from calculations done both by Dr. Corradini as well as by Dr. Liquori, there is a question about whether such a conformation would be permitted. I think the calculations were done for something like polypropylene. Whether there is any difference in chlorinated compounds like those studied in our work or not is another question. However, the indication is that such a structure would be of high energy in comparison with all of the other allowable structures such as the isotactic helices, the syndiotactic planar zig-zag and one or two modifications of it. But unless the model compound correlations can be adequately shot down, at the moment it would seem to indicate that we have to acknowl-

edge a structure like the one we see in the 2-chlorobutane and in all of the model compounds.

S. Califano (*Universita di Napoli, Naples, Italy*): By looking at the small model molecules you have shown in your slides, I noticed that only in one case you see the S'_{HH} band. In some other molecules, where one does expect such a structure you don't see the S'_{HH} band.

S. Krimm: In that list of 13 compounds shown in Table I there are 6 which show an S'_{HH} band and 4 which should but do not. However all the model compounds containing bromine and having the same structure as that of the chlorinated models for which we did not see the S'_{HH} band do show the S'_{HH} band. This fact makes us think that in the chlorinated case S_{HH} may overlap S'_{HH}.

S_{HH} is a very strong band and S'_{HH} is a rather weak one so it could very easily get lost. But the separation between the two is greater in the brominated compounds and we see this band in all of the brominated compounds.

F. Ciampelli (*Montecatini, S.P.A., Milan, Italy*): Is there any crystal splitting in PVC?

S. Krimm: The evidence so far would indicate that there is no crystalline field splitting. There are, it is true, two molecules in the unit cell of polyvinyl chloride but all of the splittings that one finds are apparently intramolecular, so these two bands that you see are due to intramolecular interactions. So far there has been no good evidence of any intermolecular effect in PVC.

P. Corradini: Calculations based on statistical thermodynamics have shown that for amorphous syndiotactic polypropylene there are about three TT sequences alternated with one GG sequence. The ratio is 3:1.

These results have been obtained for the syndiotactic polymer by assuming no energy difference between TT and GG conformations. In the case of PVC because of the existence of a chlorine atom in a gauche conformation we should expect the TT conformation to be more stabilized in comparison to the GG structure. According to the literature the energy difference should be of about one kilocalorie. Even if I did not carry out any calculation on PVC I think that such an energy difference could give rise to a model in which TT sequences in the syndiotactic polymer may be as long as 8 or 9 units. In the case of a crystalline polymer such TT sequences could give rise to a pair of bands at 610 and 638 $cm.^{-1}$.

S. Krimm: Well, perhaps one might say the following: I don't know whether we know yet how long the TT sequence has to be in order to get this 602 to 640 $cm.^{-1}$ splitting. To put it differently, I don't know that we, at the moment, know (and this is a very intriguing, interesting, and important problem) how the splitting is a function of the sequence length. I would think that structures like those that I have discussed occur primarily in a non-crystalline part of the polymer. There would be a distribution of lengths and with the distribution of length, there might be a distribution of splittings. Such a splitting may probably be the largest in the longest sequence length. However, that does not seem to be the case here. One does not find that these bands are terribly broad and smeared out; the 610 and 638 $cm.^{-1}$ bands seem to be rather respectable bands just like any other bands. But more than that I am worried at your explanation because in unoriented samples prepared in different physical states, we can make a drastic change in the relative intensities of these two bands while we have been able to find no frequency changes. I somehow feel that if these bands were associated with such a sequence, their relative intensity would stay constant. In other words, they should correspond to in-phase and to out-of-phase vibrations of carbon chlorine stretching. Why would one anticipate a change in their relative intensity with change of physical state? This change in relative intensity would seem to indicate that they have no correlation with one another in this type of interaction effect. Moreover, Dr. Corradini's calculations, as I understand them, pertain to solution and in solution one could quite reasonably expect a rather different situation than in the solid polymer. To give you a simple example, if I put PVC into solution the 638 $cm.^{-1}$ band disappears completely or almost completely and

the 610 cm.$^{-1}$ band does not. If you melt the polymer, as Dr. Shimanouchi has shown, the 638 cm.$^{-1}$ peak disappears almost completely and yet in the cast film the 638 cm.$^{-1}$ band is stronger than 610 cm.$^{-1}$. So there are drastic intensity changes at 638 cm.$^{-1}$, with no change in position of 610 cm.$^{-1}$. The same changes occur also between the solution and the solid film. In the solid I would expect that there are many more constraints on a polymer chain that prevent it from taking up an equilibrium distribution of conformations of the same form as in solution. It simply has to bend and twist in certain ways. Maybe there are certain aspects of the texture of such a folded chain structure in PVC that requires this type of constraint.

I think at the moment it is very hard to see how the correlations of these two bands with such TT sequences could be allowed.

T. Shimanouchi (*Department of Chemistry, Faculty of Science, The University of Tokyo Tokyo, Japan*): In the work we have done on PVC we had found two kinds of bands for PVC in the 600–640 cm.$^{-1}$ region. We have thought that one was originated from C—Cl stretching of crystalline syndiotactic PVC and the other from the C—Cl stretching of the amorphous or atactic PVC. Dr. Krimm has studied in more details such a compound and he has found three kinds. The problem is to find the origin of such a new band. I think that this new band may originate from some intermediate structures in the syndiotactic or atactic polymer.

S. Krimm: There is certainly another band. Perhaps I did not make it sufficiently clear; at least our present thinking is that this band does originate in the atactic portion of the polymer which perhaps would be most likely to occur in the non-crystalline regions. I'm a little worried about the arguments in terms of the model compound because it seems to me that they will take up conformations in solution which do not have the kinds of restrictions that are imposed on long-chain molecules in the solid state. We always have to keep in mind that there may be something additional which we can't find out by examining a small molecule in a liquid state. This is the only thing I can say at the moment about that. I'm not really certain about exactly what portion or what kind of a structure this band comes from. It may either come from a relatively long syndiotactic sequence that happens to find itself in a non-crystalline region and gets twisted or from a short syndiotactic sequence that finds itself between two isotactic sequences and therefore takes up this conformation. I think the thing that it is necessary to be certain about is the kind of a conformation this band is associated with. Is it associated with the S'_{HH} type of structure or not? If we can be sure of that, then we can begin to ask what kinds of chain configuration (i.e., atactic or isotactic or syndiotactic) would give rise to this isomeric structure. At least the point I'm trying to make at the moment is that there is a conformation called S'_{HH} which occurs in the model compounds and which seems to correspond to what is found in the polymer. Now exactly what part of the chain gives rise to it other than the isotactic regions, I don't know for certain at the moment.

T. Miyazawa (*Institute for Protein Research, Osaka University, Osaka, Japan*): Prof. Krimm noticed some special differences between cast film and pressed film of PVC and he interpreted them in terms of the differences in proportions of different conformations. Now I wonder if there might be some effects coming from the preferred orientation of the chains in those cast films and also in pressed films.

S. Krimm: If there were a preferred orientation effect then there could be changes in relative intensity. The maximum difference occurs between the cast film and the KBr disk, where one does not think that there might be orientation effects that would influence relative intensity. Furthermore the spectrum of the unoriented cast film has a band closer to 693 cm.$^{-1}$ whereas the oriented cast film shows a peak at 685 cm.$^{-1}$. The former band is parallel and the latter is perpendicular.

If we orient a random set of dipoles perpendicular to the stretching direction we should expect a decrease in intensity, since the number of dipoles interacting with the radiation before orientation is $^2/_3$ of the total whereas after it is $^1/_2$. On the other hand if we orient such a set parallel to the stretching direction the intensity should increase since after orientation all dipoles can interact with the radiation. In fact, it is the perpendicular

band which is enhanced in intensity when I go from the unoriented to the oriented film. Here is a case where I would expect the maximum effect of orientation and it seems not at all to go in that direction. I can't answer for certain about the pressed film. It is conceivable (we did not check this thoroughly enough) that there is a small amount of planar orientation in the pressed film compared to the cast one; but judging from the cast film versus the KBr disks, the pressed film seems to be in the same direction.

T. Miyazawa: I would just like to mention that the obvious stable chain conformations of polymers correspond to the stable conformations as found from low molecular weight compounds. Now I would also anticipate the predominant existence of the stable conformations even in non-crystalline regions. Of course we have not known the exact conformations in non-crystalline region to a certain extent but apparently more extended studies are necessary.

S. Krimm: This is certainly true, but I think one has still to keep in mind that what we call stable and what we call not stable may change. The relative numbers may change as one goes from one state to another. (Miyazawa: I would say more stable and less stable, all right?) I think there is nothing that I have said that is inconsistent with that. Assuming the correct interpretation of the weak band at 630 cm.$^{-1}$, there is a small amount of S'_{HH} in 2-chlorobutane. So unless we have got that completely wrong, that is, if we have misassigned that weak band as one of the rotational isomers, the S'_{HH} structure is present in the model compound. I don't see why one wouldn't expect at least something like that to be present in the polymers. I'm not implying that the less stable form in the liquid or in the model compound suddenly becomes the more stable form in the solid. It's just that there is a small amount of this less stable form even in the model compounds. We find a greater or smaller amount of this in the solid as well. Whether there are other factors which change the ratio of these isomeric structures in the solid, remains to be determined.

T. Miyazawa: As for the low frequency spectra of the low molecular weight compounds I want to point out that the far IR spectra are extremely sensitive to the changes in conformation.

We expect a significant improvement in this study by correlating the frequency and the conformation in the far infrared. In fact, we have found that the infrared absorption of polyglycine is extremely sensitive to the changes in conformations (from polyglycine I to polyglycine II). So in PVC and other polymer I'd expect that the far infrared spectra will be useful for studying the non-crystalline structures.

S. Krimm: I think that is quite correct and worth extra emphasis. We have, as I showed on other slides, seen the differences in the spectra, but we haven't analyzed them in detail because we have yet to do the model compounds in those spectral regions and try and get some ideas as to the origins of the bands.

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Raman Spectra of Polymers

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While infrared spectroscopy has yielded a great deal of information about the molecular and crystalline structure of many high polymers, Raman spectroscopy has so far not been widely used or been very helpful in the investigation of polymers. The main reason is that it has generally been quite difficult to obtain their Raman spectra.

However, efforts to overcome the difficulties facing the Raman spectroscopy of polymers would be very worthwhile, not just because polymers are so complex that one can never have too many data to elucidate their structure, but more particularly because knowledge of the Raman spectrum is often required for a detailed interpretation and full exploitation of the infrared spectrum. Thus, in the case of crystalline linear polyethylene, most of the observed infrared bands are combination bands, and the only binary combinations that can occur in the infrared spectrum are those of a Raman-active and an infrared-active fundamental. To interpret these, and also some of the ternary combination bands, one must know the Raman-active fundamentals.

I shall describe the limited amount of work that has been done so far on the Raman spectra of polymers. I shall point out what the difficulties have been and shall report some efforts being made to overcome these difficulties. Finally, I shall try to estimate what advances we may expect in the near future.

The first Raman spectrum of a polymer, I believe, was obtained by Signer and Weiler at Freiburg.[1] They prepared samples of polystyrene by heat polymerization of very pure styrene at temperatures below 150°C. and in the absence of oxygen. These samples were colorless, bubble-free, and as clear as glass. Their Raman spectrum was obtained by the technique used for liquids, and it was as free of background as the Raman spectra of liquids usually are.

By comparing the Raman spectrum of polystyrene with those of styrene and ethylbenzene, Signer and Weiler were able to ascribe certain bands to the phenyl groups and others to the chain. Their results confirmed Staudinger's concepts of the structure of polystyrene and indicated that intermolecular forces are weak in this polymer.

In the Raman spectrum of polystyrene produced by catalysis they observed a strong continuous background. They found that this background

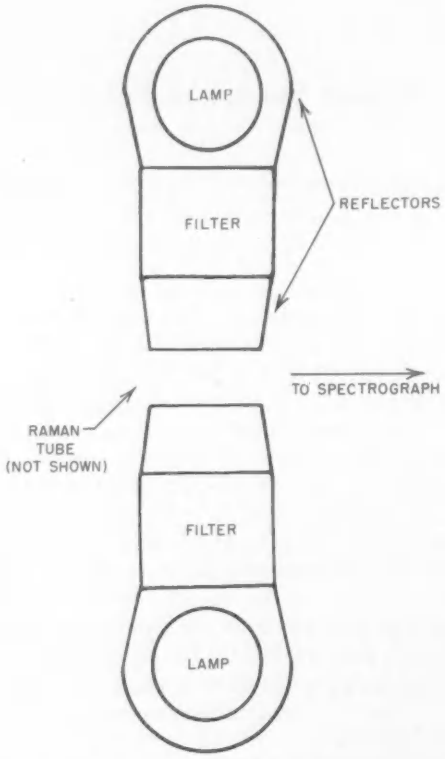

Fig. 1. Raman irradiation apparatus for crystal powders (schematic).

was not reduced when the viscosity of the polymer was diminished by dilution, and they ascribed it to fluorescent impurities. When polystyrene was formed by heat polymerization at 200°C. or when polystyrene formed at 100°C. was heated to 200°C., it was found to be fluorescent, and a strong background appeared in the Raman spectrum. To prepare a satisfactory sample of polystyrene they cooled the pure styrene to −80°C. in a glass ampule before sealing it off. Otherwise, the small amount of vapor decomposed at the seal would make the sample strongly fluorescent.

Nearly twenty years later Palm[2] extended the work of Signer and Weiler by measuring the depolarization ratios of a number of the Raman bands of polystyrene. She used the two-exposure method of Crawford and Horwitz.[3] Although her monomer sample was free of inhibitor and was distilled under reduced pressure, and although she carried out the heat polymerization in stages at temperatures not exceeding 135°C., considerable continuous background was present in all of her spectra, and the Raman bands were fairly broad and diffuse. This led her to doubt the validity of

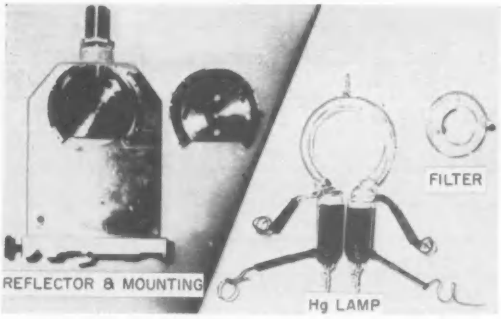

Fig. 2. Lamp, filter jacket, and housing for irradiation apparatus for crystal powders.

Signer and Weiler's explanation of the background. On the other hand, she confirmed their finding that viscosity as such is not responsible for the background.

Our work at Oklahoma was stimulated by Professor Natta's discovery of stereospecific polymers. It was motivated in part by a desire to interpret the so-called "crystallinity band" at 1894 cm.$^{-1}$ in the infrared spectrum of linear polyethylene. It was fairly clear that this band is a binary combination band, and since the space group of crystalline polyethylene includes an inversion, it would have to be a combination of an infrared-active, or of the single inactive, unit-cell fundamental and a Raman-active fundamental. At that time (1955) only four of the five infrared-active fundamentals were known, and no Raman data for polyethylene were available. It is true that some of the Raman-active fundamentals of polyethylene could be inferred by extrapolation from the Raman spectra of solid normal paraffins obtained by Shimanouchi and Mizushima.[4] However, it was not possible on this basis to interpret the band at 1894 cm.$^{-1}$.

We therefore made a considerable effort to obtain the Raman spectrum of polyethylene. Phillips Petroleum Company kindly provided us with samples of polyethylene and other substances having long methylene chains. We used an irradiation apparatus that had been built previously for work on crystal powders. It is shown schematically in Figure 1. The annular low-pressure mercury lamp is mounted in an aluminum housing with polished inner surfaces shaped so as to concentrate a maximum of light on an 8 mm. wide Raman tube placed coaxially with the lamp. An annular filter jacket, filled in most cases with a sodium nitrite solution, is placed between the lamp and the Raman tube. The lamp, the filter jacket, and the housing are shown in Figure 2. Cooling of the lamp barrel and the filter jacket was provided by blowing air through the entire assembly.

Samples of normal octacosane (n-$C_{28}H_{58}$), normal hexatriacontane (n-$C_{36}H_{74}$), octadecanoic acid, and Venezuela wax were received in the form of fine crystalline powders and were exposed in this state. Venezuela wax is

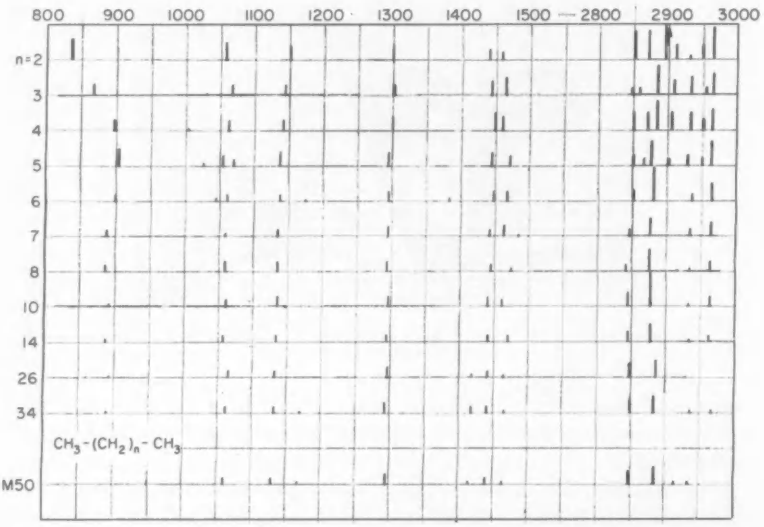

Fig. 3. Raman frequencies of solid normal paraffins and Marlex 50. Data of Nielsen and Woollett.[5]

believed to contain almost exclusively straight-chain paraffins with 25–40 carbon atoms. The polymers were received in the form of extruded, slightly translucent pellets. Marlex 20 was crushed into a fine powder with a mortar and pestle. DYNH and Marlex 50 were too "horny" to be crushed and were chopped into very small pieces with a razor blade.

The samples were then packed tightly in the Raman tube, and a length of 2 cm. or less was irradiated. To reduce the amount of unmodified mercury light emerging from the window of the Raman tube to a minimum, the window and a short part of the front of the Raman tube were carefully shielded from the incident mercury light. Considerable effort was required to determine for each sample how much of the front end of the Raman tube it was necessary to shield.

The Raman spectra were photographed with a three-prism glass spectrograph of reciprocal linear dispersion 15 A./mm. at 4358 A. and a camera of speed F/3.5. Typical exposure times ranged from 5 to 100 hr.

The results for n-$C_{28}H_{58}$, n-$C_{36}H_{74}$, and Marlex 50 are correlated with those of the lower solid normal paraffins in Figure 3. The Raman band near 890 cm.$^{-1}$ found in the normal paraffins is not observed in polyethylene. It is now ascribed to the methyl endgroups. Otherwise, the Raman spectrum of polyethylene is remarkably similar to those of the long-chain normal paraffins. The bands at 1168 and 1415 cm.$^{-1}$ had not been observed by Shimanouchi and Mizushima, who studied the Raman spectra of normal paraffins up to hexadecane. These bands in polyethylene were interpreted as $b_{1g}{}^{F}$ and $b_{2g}{}^{F}$ factor group fundamentals ascribed to

TABLE I

Raman Spectra of n-$C_{28}H_{58}$, n-$C_{36}H_{74}$, Stearic Acid, Venezuela Wax, and Three Polyethylenes

Frequency cm.$^{-1}$, and intensity[a]							
			Venezuela wax				
n-$C_{28}H_{58}$ (crystalline powder)	n-$C_{36}H_{74}$ (crystalline powder)	Stearic acid (crystalline powder)	Crystalline powder	Liquid	DXH (chopped solid)	Marlex 20 (crushed solid)	Marlex 50 (chopped solid)[b]
893 vw	890 vw						
		1042 vw?		~954 vw?			
1066 m	1063 m	1062 m	1056 m			1065 m	1061 m
				1083?			
1133 m	1133 m	1130 m	1135 m			1132 m	1131 m
~1170 vvw	1171 vw	1170 vw	1170 vw?	~1177 vw?		1171 vw	1168 vw
1297 s	1294 s	1298 s	1296 s	1303 m,b	1296 vw	1295 s	1295 s
		1377 w					
1419 w	1418 m	1412 m	1418 w			1419 w	1415 w
1442 m	1441 m	1439 m	1435 m	1434 m,b		1441 m	1440 m
1465 w	1466 w,b	1464 w	1460 w			1464 w,b	1464 w,b
2725 vw	2721 vw,b					2722 vvw	~2720 vvw?
2849 vs,b	2850 vs,b	2849 vs	2845 vs,b	2851 vs	2845 w	2847 vs,b	2848 vs, b
2886 vvs	2884 vvs	2885 vvs	2888 vs	2895 s,b	2884 w	2883 vvs	2883 vvs
						2908 w	2912 w
	2936 w,b	2928 m,b	2936 w	2937 s,b		2832 w	2932 w
	2966 w						

[a] The following abbreviations have been used: vvs, extremely strong; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, extremely weak; b, broad.

[b] An almost identical Raman spectrum was obtained of hydrogenated Marlex 50.

methylene rocking and wagging, respectively. The bands at 1061 and 1131 cm.$^{-1}$ were interpreted as a_g^F and b_{2g}^F skeletal deformation modes. The band at 1295 cm.$^{-1}$ was ascribed to methylene twisting of species b_{3g}^F and that at 1440 cm.$^{-1}$ to methylene deformation (a_g^F). The strong Raman bands at 2848 and 2883 cm.$^{-1}$ were interpreted as symmetrical and unsymmetrical C-H stretching of species a_g^F and b_{1g}^F, respectively. The rather broad and diffuse band at 1464 cm.$^{-1}$ and the weak bands at 2912 and 2932 cm.$^{-1}$ are probably caused by amorphous polyethylene, although overtones should also occur near these positions.

The observation of the Raman band at 1168 cm.$^{-1}$ led immediately to the interpretation of the "crystallinity band" at 1894 cm.$^{-1}$ as a binary combination of the b_{2u}^F and b_{1g}^F methylene rocking fundamentals, 726 + 1168 = 1894 (B_{3u}^F). The observed Raman spectrum of polyethylene, together with determination of the dichroisms of the infrared bands, proved very useful in explaining a large number of infrared combination bands.[6]

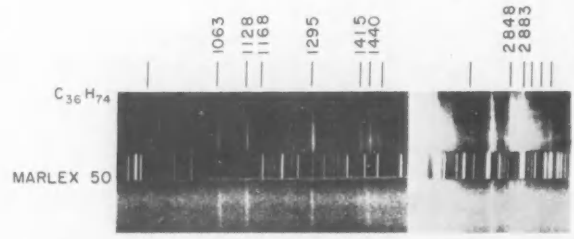

Fig. 4. Raman spectra of solid n-$C_{36}H_{74}$ and Marlex 50. Data of Nielsen and Woollett.[5]

Table I shows all of the Raman bands observed by us. All of these bands were obtained as shifts from the 4358 A. mercury line. For n-$C_{36}H_{74}$ and Marlex 50, the 2850 and 2883 cm.$^{-1}$ bands were also observed as shifts from the 4047 A. line. With the sodium nitrate solution replaced by water in the filter jacket, the additional Marlex 50 bands at 1061, 1131, and 1295 cm.$^{-1}$ were observed as excited by the 4047 A. line. The Raman spectrum of a sample of hydrogenated Marlex 50 could not be distinguished from that of Marlex 50. Hence, it is not included in Table I. It is a peculiar fact that no splitting of Raman bands was observed. The reason may be, as first suggested by Krimm,[7] that only the more intense of two components was observed.

Considerable background was encountered in all of the spectra, especially in those of the polymers. This may be seen in Figure 4. The background is caused, at least in part, by fluorescent impurities. We tried to reduce the fluorescence by washing the powders with carbon tetrachloride and other solvents but attained only a small reduction in the fluorescence and the background. The fact that the background is strongest where the weak continuum occurs in the spectrum of the mercury lamp

indicates that it is not caused exclusively by fluorescence but may result in part at least, from colloidal impurities or inhomogeneities in the samples.

We made many attempts to obtain the spectra of the samples in the liquid state, but in all cases a strong continuous background was obtained, and only for Venezuela wax were any Raman bands observed other than the two or three strongest. Because of the great viscosity of the molten polyethylenes it was not possible to make them fill the Raman tube uniformly. The much stronger background obtained with the seemingly transparent liquids than with the translucent solids is rather puzzling.

In the fourth column of Table I are listed the Raman frequencies observed for liquid Venezuela wax. The Raman band ascribed to methylene twisting, which occurs at 1296 cm.$^{-1}$ in the solid, appears to be shifted to 1303 cm.$^{-1}$ in the liquid. This is the position of an infrared band found in amorphous, but not in crystalline, polyethylene. Thus, lack of crystallinity appears to shift this band and render it infrared-active. The doubtful band at 1083 cm.$^{-1}$ also corresponds to a broad infrared band of amorphous polyethylene.

Some time after we had studied the Raman spectrum of polyethylene we made an effort to obtain the Raman spectrum of polytetrafluoroethylene (Teflon). The sample was cut from the stock in our shop. The continuous background was even greater than in the case of polyethylene. However, we observed the following eight Raman bands, two of which are not quite certain: 225 vvw?, 292 vw, 385 vw, 733 m, 995 vw?, 1226 vvw, 1304 vw, 1382 w.

The chain in polytetrafluoroethylene is helical with 13 or 15 CF_2 groups in the identity periods.[7] The Raman-active fundamentals have been inferred from data on n-C_7H_{16} and from infrared combination bands.[8] The Raman band observed at 1382 cm.$^{-1}$ is undoubtedly a totally symmetric CF_2 stretching fundamental and the band at 733 cm.$^{-1}$ a CF_2 deformation fundamental of the same species. The much weaker band at 292 cm.$^{-1}$ may be an a_1 fundamental associated with CF_2 twisting. The Raman band at 385 cm.$^{-1}$ has a counterpart in the infrared spectrum which has been ascribed to the amorphous phase.[7] The band at 1226 cm.$^{-1}$ is probably also caused by C—F stretching. It lies midway between the two strongest bands in the infrared spectrum, at 1210 and 1242 cm.$^{-1}$, assigned to species a_2 and e_1, respectively.[7] It is probably a CF_2 stretching fundamental of species e_2. We hope to check and extend these observations on a pure sample and have therefore not published these results. However, our attempts to secure a better sample have not yet been successful.

In 1958 Simon, Mücklich, Kunath, and Heintz at the Technische Hochschule, Dresden, published the results of an extensive spectroscopic investigation of poly(vinyl acetate), poly(acrylic acid), and poly(ethyl acrylate).[9] They do not give any details of their irradiation apparatus but presumably it was that described earlier.[10] They reproduce some very fine Raman spectra. Figure 5 shows their spectra of acrylic acid (H_2CCH-$COOH$), poly(acrylic acid), ethyl acrylate ($H_2CCHCOOCH_2CH_3$), and

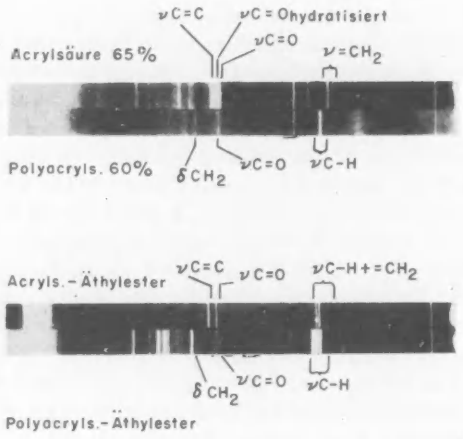

Fig. 5. Raman spectra of acrylic acid, poly(acrylic acid), ethyl acrylate, and poly(ethyl acrylate). Data of Simon et al.[9]

poly(ethyl acrylate). The most complete Raman spectrum of poly(acrylic acid) was obtained of a 60% mixture with water. Although samples of anhydrous poly(acrylic acid) were obtained which were as clear as glass, their Raman spectra had a strong background. No information is given about the sample of poly(ethyl acrylate), but it was presumably anhydrous.

The authors followed the slow polymerization of vinyl acetate over a year and a half by periodic observations of the Raman spectrum. They showed, among other things, that hydrogen bonding of carboxyls occurs in poly(acrylic acid). Their interesting results could hardly have been obtained without Raman spectroscopy. On the other hand, their work shows that, even with these rather favorable polymers, considerable attention must be given to sample preparation if good Raman spectra are to be obtained.

Some four years ago, Tobin[11] developed a crystal powder technique which differed from that used by us mainly in the following respects. His Toronto-type mercury lamp was of helical shape with four turns. Instead of a nitrite solution he used two rather elaborate chemical primary filters which not only cut out mercury light of wavelengths below 4358 A. but also absorbed from 4400 to 5400 A. The light scattered by the sample was reflected by two interference filters transmitting 4358 A. before entering the slit of the spectrograph. In this manner the 4358 A. line was effectively removed from the observed spectrum. The spectrograph was a fast grating instrument.

Tobin used this technique to obtain the Raman spectra of DYNH, Marlex 50 and isotactic polypropylene. Figure 6 shows, rather poorly, his spectra of the polyethylenes. These spectra have less background

Fig. 6. Raman spectra of DYNH and Marlex 50 polyethylenes. Data of Tobin.[11]

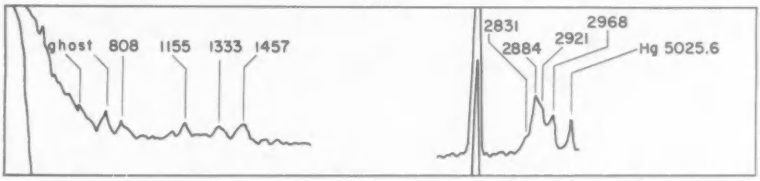

Fig. 7. Raman spectrum of isotactic polypropylene. Data of Tobin.[12]

than those obtained by us, and the exposure times were 15 to 50 times shorter. Tobin confirmed our Raman frequencies but did not find any additional bands. He did not observe any splitting, although he states that splittings as small as 3 or 4 cm.$^{-1}$ could have been detected. Figure 7 shows a tracing of the Raman spectrum of isotactic polypropylene observed by Tobin.[12] The continuous background is quite strong.

Tobin interpreted the Raman bands at 808 and 1157 cm.$^{-1}$ as skeletal vibrations of tertiary methyl groups. The band at 1333 cm.$^{-1}$ he ascribed to C—H bending and that at 1457 cm.$^{-1}$ to asymmetrical methyl deformation superposed on methylene deformation. The four bands near 2900 cm.$^{-1}$ he ascribed to symmetrical and asymmetrical C—H stretching in methylene and methyl groups. Several Raman-active fundamentals evidently remained unobserved. Tobin states that fluorescence was the limiting factor both for polyethylene and polypropylene. He also attempted to obtain the Raman spectrum of polytetrafluoroethylene but got only a continuous background.

Two years ago, six Japanese scientists, Tadokoro, Kobayashi, Kawaguchi, Sobajima, Murahashi, and Matsui, published a normal coordinate analysis and a Raman spectrum of polyoxymethylene $(CH_2—O—)_n$, or paraformaldehyde.[13] They obtained the spectrum shown in Figure 8 but do not give any details about how it was obtained. The continuous background is very strong. The sample was highly purified. They remark that commercial samples gave very poor spectra, probably because of fluorescence.

Very recently Brown[14] reported the Raman spectra of polyethylenes obtained with a Cary Model 81 photoelectric Raman spectrograph. He used the standard irradiation apparatus designed for liquid samples. That one can get fair Raman spectra of certain solid substances in this manner is well known and has recently been demonstrated for the Cary 81 by Ferraro, Ziomek, and Mack.[15]

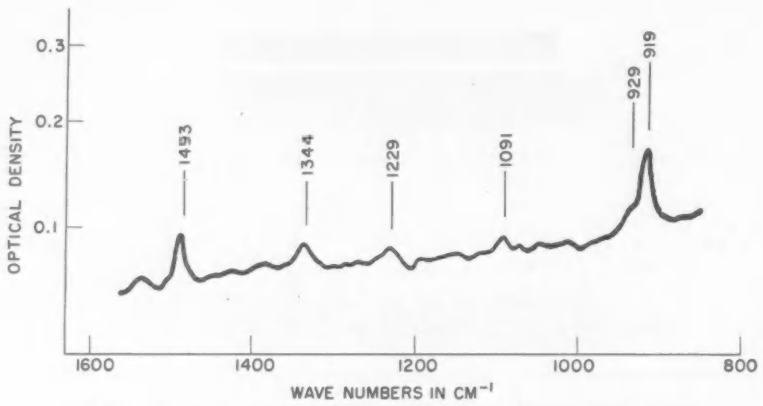

Fig. 8. Raman spectrum of polyoxymethylene. Data of Tadokoro et al.[13]

The polyethylene samples used by Brown were long cylindrical rods of 7 mm. diameter placed inside a windowless Raman tube in such a manner that not only the cylindrical sides but also the front end surface were illuminated. Masking indicated that about 13 mm. of the length of the rod contributed Raman scattered light to the spectrograph and that illumination of the front end enhanced the Raman bands considerably.

The specimens were either molded in the Raman tube or machined from extruded rods. The latter procedure gave a more satisfactory spectrum.

The upper part of Figure 9 shows the Raman spectrum of a branched polyethylene with 3 methyl groups per 100 carbon atoms obtained in this manner. All but one or two of the Raman bands observed photographically by us can be seen here. The resolution appears to be somewhat lower

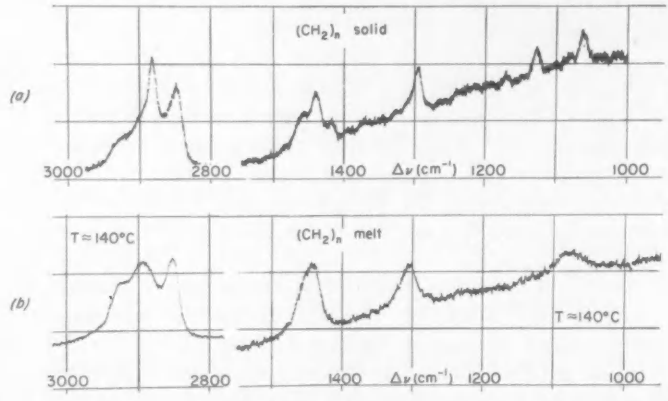

Fig. 9. Raman spectrum of solid and molten polyethylene. Data of Brown.[14]

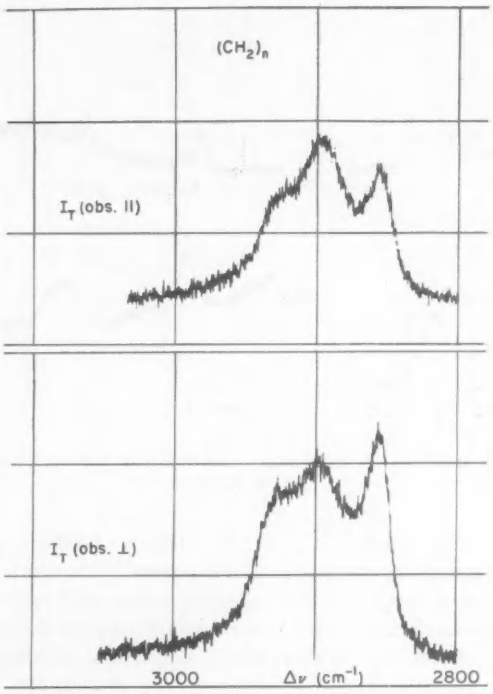

Fig. 10. Raman spectrum of molten polyethylene obtained with polarized incident radiation. Data of Brown.[14]

than that obtained by the photographic method. However, the time and effort required to obtain such a spectrum with the photoelectric Cary 81 spectrograph is, of course, considerably less.

In the lower part of Figure 9 is shown the Raman spectrum obtained by Brown of molten polyethylene. This was obtained simply by heating the rod electrically with a wire wrapped around the Raman tube. Because of the high viscosity of the molten polymer very little flow occurred, and no window was required to confine the sample. The amplification used in this case is much lower than for the solid, and the continuous background is more intense.

This Raman spectrum of liquid polyethylene is considerably superior to what we were able to obtain. One reason is undoubtedly the fact that Brown melted a solid rod, while we melted a finely chopped sample and were unable to remove small air bubbles. Another reason may be the absence of a window in Brown's Raman tube. It is quite possible, however, that the difference in background is caused by unknown differences in the purity or morphology of the samples.

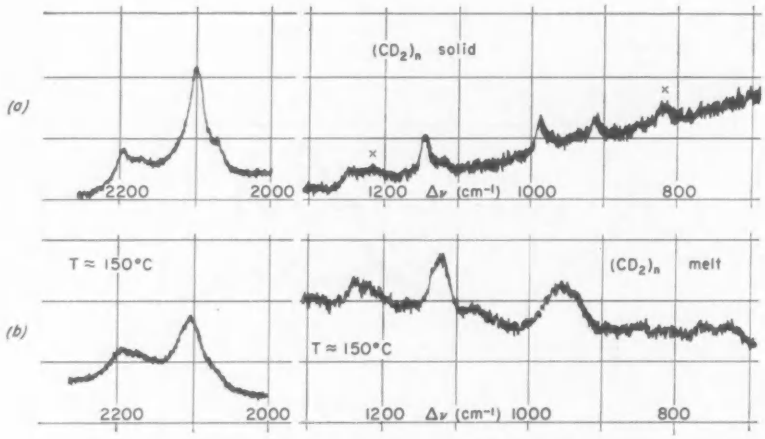

Fig. 11. Raman spectrum of deuterated polyethylene in the solid and molten state. Data of Brown.[14]

It is interesting to note the shift from 1295 to 1303 cm.$^{-1}$ in the band ascribed to methylene twisting. This agrees with what we found for Venezuela wax. Also the broad band at about 1080 cm.$^{-1}$ agrees with that found in the liquid wax. As already mentioned, infrared bands are found in these positions in amorphous and liquid polyethylene and in long-chain normal paraffins.

Figure 10 shows a part of the Raman spectrum of molten polyethylene obtained with polarized incident light. The symmetric CH_2 stretching band at 2848 cm.$^{-1}$ is partly polarized, as expected. In crystalline polyethylene there are two unit cell fundamentals here, of which one should give a polarized and the other a depolarized Raman band. In an isolated straight polyethylene chain there is an a_g^F fundamental which should be polarized in the Raman spectrum. In the molten polyethylene the chains are undoubtedly somewhat bent, but still the Raman bands associated with symmetrical CH_2 stretching should be largely polarized. The band, or rather the unresolved bands, near 2930 cm.$^{-1}$ are also partly polarized, which is in accord with the assumption that there is an overtone here, presumably of the infrared active methyl deformation at 1468 cm.$^{-1}$.

Figure 11 shows the Raman spectra of completely deuterated polyethylene in the solid and molten states. The sample was polymerized by a high-pressure process and was probably branched. The spectra are not quite as good as for ordinary polyethylene, and two bands marked x are ascribed to impurities. However, Brown was able to identify all but two of the factor group fundamentals and to correlate them satisfactorily with those of ordinary polyethylene. Also, he was able to give a plausible interpretation of the maximum near 2200 cm.$^{-1}$ as a superposition of combination and overtone bands.

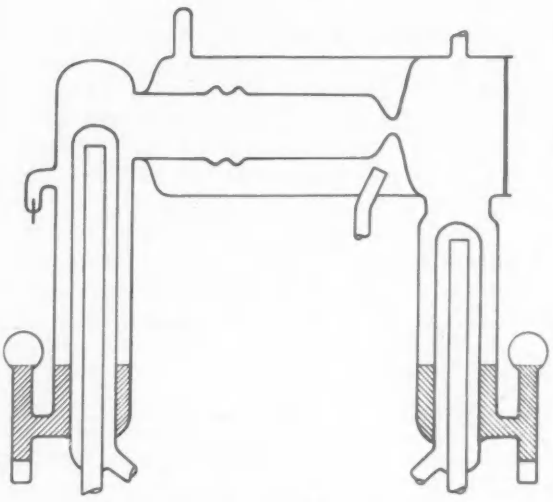

Fig. 12. Focal point Raman lamp.

Let me now venture a few remarks about the prospects for future advances in the Raman spectroscopy of polymers. Most polymers cannot be prepared as large transparent blocks but must be studied either in the form of translucent solid blocks or as fine, more or less crystalline, powders. In either case the general techniques for obtaining the Raman spectra of crystal powders should be applicable.

Although there is still some difference of opinion about the relative merits of different methods of irradiation, considerable progress has been made in recent years in crystal powder techniques. The most recent work has been done by Moser and Stieler.[16] These authors appraise earlier work in the field and give an extensive bibliography. They describe a powerful low-pressure mercury lamp with a constriction producing a "focal point" of very high luminosity. They compare different types of irradiation and conclude that back irradiation of a pellet or lateral irradiation of a cylindrical Raman tube with conical inner surface ("Kegelküvette") give the best results. More recently, Behringer[17] has proposed a modification of the former of these methods of irradiation. It is possible, of course, that the method of radiation that is most efficient for one sample may not be so for samples of different types.

At Oklahoma we are using a mercury lamp similar to that described by Moser and Stieler. Its construction is shown in Figure 12. Not only the electrode ends but most of the lamp are water-cooled, so as to reduce the continuous background as much as possible. The cross section at the constriction is about 5 mm. in diameter. The luminous intensity, of wavelength 4358 A., at the constriction increases with the current density there until the latter has reached a value of about 100 amp./cm.^{2} and then

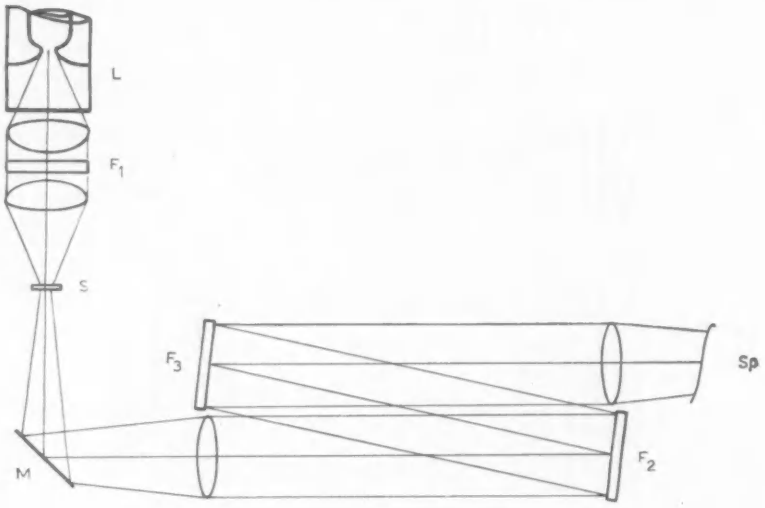

Fig. 13. Raman irradiation apparatus (schemat..).

becomes nearly independent of the current density. The window is large, so as to make it possible to utilize a large solid angle of the emission from the region around the constriction.

Figure 13 shows schematically the irradiation apparatus. Between the two condensing lenses is either an interference filter or a chemical filter which transmits the 4358 A. mercury line but cuts out both shorter and longer wavelengths. Because of the small size of the polymer crystals only a small sample can be used, and we have concluded that back-irradiation of a pressed pellet should be the most efficient and practical method of obtaining the Raman spectrum. Behind the sample the scattered light is reflected by two secondary interference filters which transmit the 4358 A. line and thus prevent most of the light of this wavelength from entering the spectrograph.

We have made only preliminary observations with this apparatus, using a spectrograph of high speed (F/1.5) and correspondingly low linear dispersion. Although we have obtained Raman spectra of polyethylene and a couple of long-chain normal paraffins, we have not as yet observed any new Raman bands.

The careful preparation of samples will undoubtedly continue to be a condition for obtaining good Raman spectra. This means that progress will depend on the close collaboration of polymer chemists and spectroscopists and also that Raman spectroscopy is not likely to become a routine, as infrared spectroscopy has become to a considerable extent.

We have spent considerable effort to eliminate the fluorescence of polyethylene samples. We first dissolved the polyethylene in hot xylene and

then precipitated and washed it with propyl alcohol. This reduced the fluorescence greatly. However, after two or three days the fluorescence reappeared, even when the polymer was kept in an evacuated container.

We found that samples of polyethylene to which no antioxidant had been added fluoresced less than other samples. A mass of minute single crystals of such a polyethylene that exhibited no observable fluorescence even after standing for many days was obtained in the following manner. A dilute solution of the polymer in xylene at 130°C. was allowed to cool slowly over several days until crystals appeared at about 74°C. These crystals were redissolved in xylene at 95°C. The new solution was cooled slowly and a multicrystalline sheath was formed at 74°C. The crystal mass was washed with ethanol and dried. Microscopic examination showed that the bulk of the crystals were of the axialite type described by Keller.[18] We have also prepared a mat of lozenge-shaped crystals from a solution in tetrachloroethylene.

It would seem to be of considerable interest to make a serious effort to determine the nature of the fluorescent impurities responsible for the continuous background in the Raman spectra of various polymers. If inhomogeneities in certain polymers are the cause of a background it would be of interest to study this background and attempt to correlate it with the morphology of the polymers.

When the continuous background is caused by the presence of one or a few fluorescent impurities, it should be possible to eliminate it by exciting the Raman spectrum by light of a wavelength that does not produce fluorescence. The use of an optical maser, or laser, for this purpose suggests itself. If the wavelength lies in the red, as in the case of a ruby laser, a grating spectrograph would generally be needed to provide satisfactory dispersion. Although Porto and Wood[19] have obtained good Raman spectra of a few compounds by means of a ruby laser, it is too early to make any predictions as to what role lasers may come to play in Raman spectroscopy; however, the role is likely to be important.

Quite apart from the experimental difficulties of obtaining the Raman spectra of polymers, it must be recognized that Raman scattering, involving two photons rather than one, is inherently less sensitive than infrared absorption. Thus, constituents present in concentrations of less than one or a few per cent will rarely reveal themselves in the Raman spectrum, and this spectrum will generally provide fewer data than the infrared spectrum. On the other hand, since Raman scattering and absorption depend on different parameters, the Raman spectrum will in many cases yield information that could not be obtained by infrared absorption. Raman spectroscopy will undoubtedly make greater contributions to our knowledge of high polymers in the future than it has in the past.

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Discussion

S. Krimm (*University of Michigan, Ann Arbor, Michigan, U.S.A.*): Would it be of any help to examine the Raman spectra of polymers which have been swollen in solvent? Have you tried it?

J. R. Nielsen: We have not tried it. Whether it would be practical or not I do not know.

S. Krimm: Is there anything which prevents one either in principle or in practice from obtaining polarized spectra of polymers? I noticed that in your work there are no polarized spectra.

J. R. Nielsen: It depends on the state of the sample. If one could produce a transparent polymer with practically all of the chains oriented, then of course one could obtain the depolarization ratios. But if one must use the crystal powder technique, I don't see any possibility of obtaining depolarization ratios. So my answer would be that it depends entirely upon the nature of the polymer. I don't think that it would be easy to obtain depolarization ratios for polyethylene, unless one can do it in the liquid state. The recent work of Brown is somewhat encouraging although his background is still so large that it is questionable whether one could get accurate depolarization ratios.

A. Elliott (*King's College, London, England*): I wonder whether it would be possible, in the case of polymers which are soluble in a convenient solvent, to use a technique similar to that used in streaming birefringence. One could flow the solution through a suitable cell in order to produce some orientation. In such a case would you then be able to employ polarized radiation?

J. R. Nielsen: That might be possible, provided one can get a sufficient concentration of the polymer.

T. Miyazawa (*Osaka University, Japan*): Have you ever observed any Raman lines due to the E_2 fundamentals of helical polymers?

J. R. Nielsen: We have done some preliminary work on Teflon, and I remember there is a line which lies between two infrared bands which might be assigned either to E_1 or E_2 fundamentals.

S. Krimm: E_1 is both Raman and infrared active; E_2 is only Raman active. The fact that it does not coincide with an infrared band might indicate that it is an E_2 fundamental.

T. Miyazawa: If that is so I believe it is the first Raman line found which is an E_2 fundamental.

T. Miyazawa: In analyzing the infrared spectra of isotactic polypropylene and polyethylene glycol, I have compared the infrared bands with the Raman lines observed by other authors. I have found that the Raman lines of isotactic polypropylene and polyethylene glycol correspond rather nicely with the perpendicular infrared bands. So far I have not seen any strong Raman line due to A fundamental of isotactic polypropylene and to A_1 fundamentals of polyethylene glycol. I wonder why these A and A_1 vibrations of helical polymers are weaker than the Raman lines due to E_1 fundamentals. For the lower molecular weight compounds we generally expect that the totally symmetric vibrations are strongest in the Raman effect. Do you have any suggestion?

J. R. Nielsen: The only suggestion I might have is the following: in determining the activity of a polymer, especially if the polymer is not completely crystalline, the local symmetry is probably more important than the total symmetry. For example a certain mode may include the symmetric vibration of a group, but this mode might not be symmetrical with respect to the whole chain.

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Some Uses of Polarized Infrared Radiation in the Spectroscopy of Polymers

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INTRODUCTION

Polarized infrared radiation was used in early work on the spectra of single crystals, mainly inorganic, and striking changes in the spectrum were observed on changing the direction of the electric vector of the incident radiation (see, for instance, Schaeffer and Matossi[1]). The first observations on the infrared spectra of polymers with polarized radiation were made by Ellis and his co-workers in the region of overtone and combination bands.[1a] Uncertainties in the interpretation of overtone spectra have caused the interest to shift to the region of fundamental vibrations, but the overtone region is still important, because there the spectra of whole fibers or fiber bundles may be observed. In the region of fundamental bands it is usually necessary to employ films or sections of monofils, because the high absorption requires the specimen thickness to be only a few microns.

POLARIZERS

Reflection

Reflection of light by a dielectric produces, in general, a partly polarized beam. The reflected beam is completely plane-polarized when it is at right angles to the refracted beam, in which case

$$\tan i = n$$

where i is the angle of incidence and n the index of refraction (Brewster's law). Any material transparent in the infrared may be used to produce a plane-polarized beam by reflection. The reflected beam has its electric vector vibrating perpendicular to the plane of incidence. If I_σ and $(I_\sigma)_r$ are, respectively, the intensities of the incident and reflected beams vibrating normally to the plane of incidence

$$(I_\sigma)_r = I_\sigma \sin^2 (i - r)/\sin^2 (i + r)$$

The component with E vector vibrating in the plane of incidence has an intensity

$$(I_\pi)_r = I_\pi \tan^2 (i - r)/\tan^2 (i + r)$$

With clean reflecting surfaces the degree of polarization produced is very high. The intensity of the reflected beam increases with the refractive index. Table I gives the index of refraction, Brewster angle, and the percentage of an unpolarized beam which is reflected at this angle, for some materials which have been used for polarizing. Reflection polarizers are inconvenient because their introduction into a beam results in a changed optical path, and, if the beam is converging, refocusing is necessary. With modern spectrometers their use is difficult.

TABLE I

Reflection of Polarized Radiation by Some Materials in the Infrared Region

Material	Refractive index	Brewster angle	Intensity of unpolarized beam reflected at the Brewster angle, %
Silver chloride	2.0	63°26′	18
Amorphous selenium	2.54	68°30′	27
Germanium	4.01	76°	39

A reflecting system of wide aperture has been proposed by Takahashi.[2] It requires to be placed in a collimated beam and is not well-suited for use in an image-forming system. A germanium reflection polarizer has been described by Edwards and Bruemmer,[3] and as may be seen from Table I the performance is high. A second reflecting surface can be introduced to bring back the beam to its original direction, but the need for refocusing after introduction of the polarizer remains.

Transmission Polarizers

A pile of glass plates inclined so that visible radiation falls on them at the Brewster angle is a well-known device for producing plane-polarized light. If the glass plates are replaced by a transparent material, the same arrangement may be used in the infrared region. The polarization produced in the refracted beam by a single reflection is not high, but quite high polarization can be produced by using a sufficient number of plates. The higher the refractive index, the fewer plates will be needed for a given degree of polarization.

Selenium Transmission Polarizers. The first infrared transmission polarizer described had selenium films as reflectors.[4,5] Selenium films (in the amorphous form) can be made a few microns in thickness, so thin that neither the sharpness nor the position of an image is appreciably affected by inserting the polarizer in a converging, focused beam. The polarizer may be rotated to change the direction of the E vector of the transmitted beam.

At the thickness employed, selenium films are fragile but with reasonable care will remain intact for a number of years. The performance of a polarizer is expressed by the percentage polarization which it produces. If the intensities of the transmitted beam with the E vector parallel and perpendicular to the plane of incidence are, respectively, I_π and I_σ, the percentage polarization is

$$\frac{I_\pi - I_\sigma}{I_\pi + I_\sigma} \times 100$$

For a selenium polarizer of six films, this quantity was found by Elliott, Ambrose, and Temple to be more than 98%.[5] The transmission of the original unpolarized beam was 37%.

It is not practicable to calculate the performance of a transmission polarizer, since the effect of multiple reflections (which is disadvantageous) depends so much on the shape of the reflecting surfaces, as well as on the optical system. Reflections from the two surfaces of a film can produce interference fringes and with uniform selenium films the effect can be pronounced. By using a selection of films of different thicknesses, and by varying the thickness within one film, these effects can be rendered inappreciable.[6,7]

Silver Chloride Transmission Polarizer. Rolled silver chloride sheet of high purity has been used for transmission polarizers.[8,9] With a six-film polarizer the percentage polarization is 92% and the transmission 52%. The thickness of the silver chloride sheets (0.002 in.), while giving robustness, is sufficient to produce an appreciable displacement of the transmitted beam, and this is troublesome when the polarizer is rotated. Various arrangements have been proposed to compensate for this displacement.[10,11]

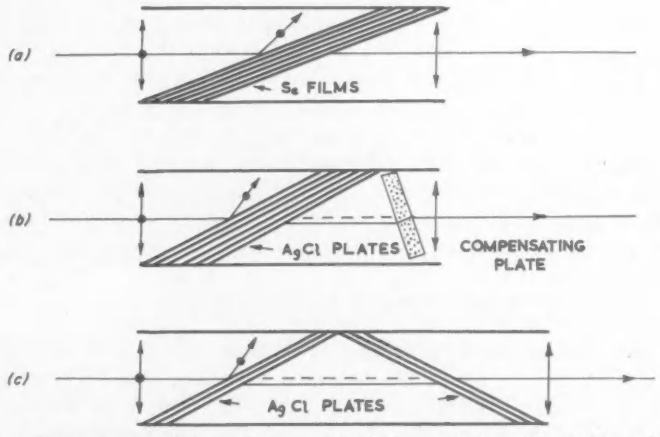


Fig. 1. Infrared transmission polarizers: (*a*) selenium polarizer; (*b*) and (*c*) methods of compensating for the image displacement introduced by silver chloride polarizers. From Fraser.[11]

The percentage polarization of a silver chloride polarizer (which is lower than that of a selenium polarizer with the same number of plates) can be increased considerably by making the plates slightly wedge-shaped and by inclining them slightly to each other.[12] The polarizer is used so that the image displacements are transverse to the slit. With a narrow source, such as a Nernst filament focused on the slit, these multiply reflected beams would not then be transmitted by the slit. However, to utilize this the polarizer must be kept fixed relative to the slit, and to examine the transmission of an oriented specimen with different directions of the electric vector it is necessary to rotate the specimen relative to the polarizer. In consequence, the specimen must be uniform in thickness and in orientation over a sufficient area, and this may be difficult to achieve. Some arrangements of transmission polarizers are shown in Figure 1.

Dichroic Polarizers

Oriented materials, such as polymers, crystals, or polycrystalline arrays, frequently show dichroism within some of their absorption bands and in extreme cases may absorb practically completely one polarized component of light incident on them. In such cases, an incident unpolarized beam emerges plane-polarized. The polarizing filter known as Polaroid HN is of this type and is an efficient polarizer in the visible region Similar polarization in the near infrared region (to 2 μ) may be obtained by using Polaroid HR. This is a polyvinyl alcohol–polyvinylene–iodine) complex with a strong absorption centered at about 1.5 μ.[13] By using different thicknesses, the range 0.7–2.8 μ may be covered.

Grating Polarizers

The fact that wire gratings have polarizing properties has long been known, and they were in fact used by Hertz[14] to produce plane-polarized radiation. Recently, Bird and Parrish[15] have made wire grid polarizers by depositing gold on the ridges of a replica grating. It is unfortunate that at present it is necessary to use a plastic replica such as polyethylene or polytrifluorchlorethylene, and the absorption bands of these materials make the polarizer useless in some regions. Apart from this, grid polarizers can be made which cover the region 2–15 μ satisfactorily. They are compact, easily rotatable, and can be used in sharply converging beams.

ORIENTATION IN POLYMERS

The fact that polarized radiation gives extra information about polymer spectra is, of course, due to the fact that most long-chain polymers are capable of being ordered to some extent, so that there is at least a preferred direction in which the chains lie. The incompleteness of this orientation restricts the information which can be obtained. Thus, in crystalline polymers the order within the crystallite may be quite high,

but many crystallites are present and they may have only one axis (generally the one corresponding to the chain axis) arranged in a common direction, and even then the crystallites are usually dispersed over a considerable angular range around this direction (the fiber axis). If the distribution of molecular chains has cylindrical symmetry with respect to the fiber axis the arrangement is optically uniaxial, and is known as fiber type orientation.

In fibers which have been rolled or pressed and often in stretched films, the cylindrical symmetry about the preferred axis may be lost, and in extreme cases the molecular chains may be almost entirely restricted to a plane, with a distribution which is symmetrical on either side of the fiber axis. In this case the polymer is optically biaxial, and has uniplanar orientation. Models for orientation in polymers have been considered by a number of authors.[11,16–21]

In the above paragraphs we have been concerned only with the orientation of the chain axis with respect to the fiber axis, and often there is no other orientation present. In some cases, however, notably when polymer chains form sheets connected by hydrogen bonds, there may be some orientation of the other molecular axes. When an oriented fiber of nylon 66 is pressed, for instance, these sheets tend to lie parallel to the pressed surfaces of the fiber. Such fibers are markedly biaxial and may show biaxial conoscopic figures;[22] they are said to be doubly oriented.

The symmetry of the individual crystallites in a polymer may be quite low (nylon 66 is triclinic) but in fibers containing large numbers of small crystallites a kind of pseudo-symmetry is introduced by the way in which they are distributed. Since the crystallites are much smaller than the wavelength of visible radiation (and still smaller compared with infrared waves) this pseudo-symmetry ensures that the optic axis of fiber-type polymers coincides with the fiber axis. With films or pressed fibers with uniplanar orientation (or double orientation) the axes of the refraction indicatrix are along the fiber axis, normal to the pressed surface and parallel to the pressed surface, the three axes being mutually perpendicular. When radiation is incident normal to the fiber axis (and also normal to the film or pressed surface if there is one), waves in which the E vector is vibrating either perpendicular or parallel to the fiber axis will be transmitted through the specimen as plane-polarized waves. These two directions of the E vector should be used, since other directions will, in general, result in a plane-polarized wave becoming elliptically polarized as it passes through the specimen.

SOURCES OF ERROR

The specimen will generally be set with its long (fiber) axis parallel to the spectrometer slit, and in this case the polarizing properties of the prism or grating will affect the intensity of the beam but will not alter its state of polarization.

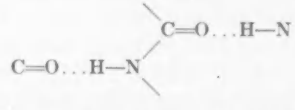
The effect of loss of intensity produced by the polarizing effect of prisms, etc. (in one direction of the E vector) when the polarizer is an imperfect one has been discussed by Charney.[23] With a polarizer in which the percentage polarization is of the order of 90%, the polarization produced by a prism can lower the measured dichroic ratio considerably, especially when the real dichroic ratio is high. This effect seems to be inappreciable with a selenium polarizer with six films, with which dichroic ratios probably in excess of 100:1 have been observed in crystals.[24] With grating spectrometers the dependence of the transmission on the orientation of the electric vector can be very great at some wavelengths, and gross errors can arise if the degree of polarization of the polarizer is not high enough.

If a micro-illuminator or reflecting microscope is used for examining small structures, the polarizer will be put in the uncondensed part of the beam to avoid the effect of a strongly convergent beam. If space is available, the polarizer may be put immediately behind the exit slit, provided that rotation of the polarizer does not displace the image on the detector. The convergence of the radiation beam within the specimen has the effect of lowering the observed dichroism. Theoretical treatments of this effect by Fraser[25] and by Wood and Mitra[26] suggest that in fibers the effect is small. In crystals the effect can be important if the transition moments of the bands measured are not in the plane normal to the axis of the radiation cone.

POLYAMIDE SPECTRA

The structure of the Amide I band at ca. 1640 cm.$^{-1}$ in some polyamides provides an interesting example of the effect of interactions between identical monomer units in a polymer[27] and shows how polarized radiation may be used to reveal hitherto unobserved, weak bands.

The strong bands in the infrared spectra of polyamides (nylons) are associated with vibrations of the amide group



in which the carbonyl oxygen atom is connected by hydrogen bonds to the NH group in a neighboring chain. The vibrations of the amide group are to some extent shared by all the atoms, but those responsible for the strongest bands reside chiefly in either the C=O or the NH group. Thus, the strong band at ca. 3300 cm.$^{-1}$ is mainly due to vibrations in which the NH bond is stretched and has a transition moment approximately along this bond (the transition moment direction coincides with the direction of the electric vector of the incident radiation for which absorption is maximum). If an oriented film or a thin longitudinal section of nylon is examined spectroscopically with polarized radiation, maximum absorption will occur when the E vector is perpendicular to the chain axis (see

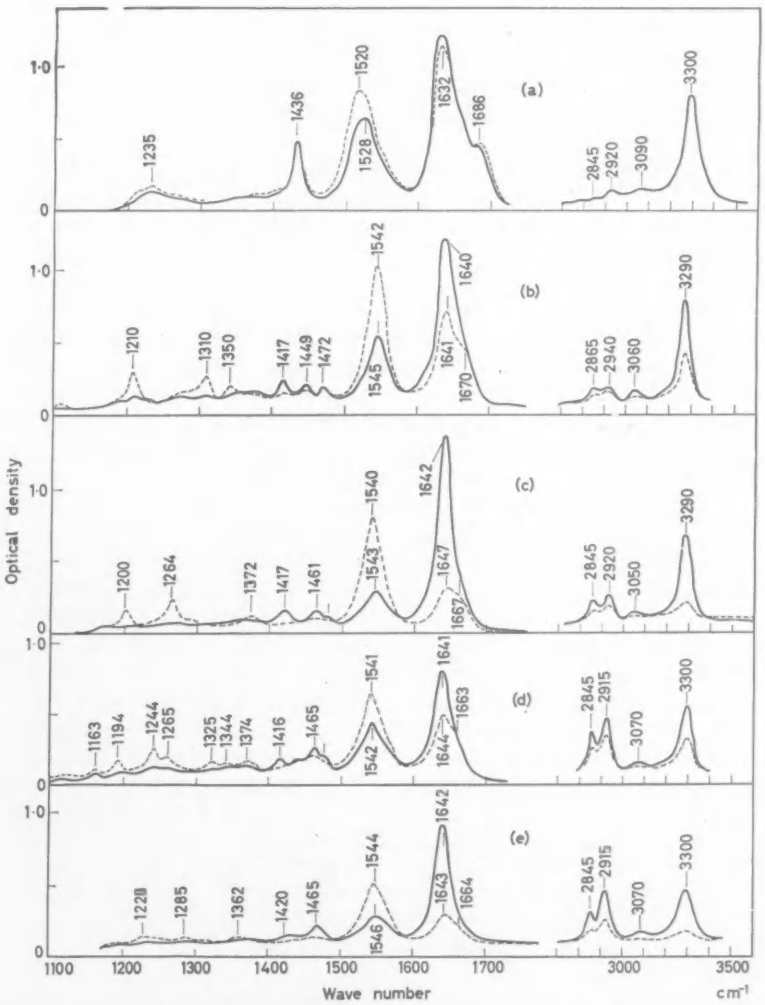


Fig. 2. Infrared spectra of oriented polyamides in (α,β) form: (——) E vector perpendicular to fiber axis; (- - - -) E vector parallel to fiber axis; (a) nylon 2 (polyglycine), 3 μ region shown for unoriented polymers; (b) nylon 4, (c) nylon 6, (d) nylon 8, (e) nylon 10. From Bradbury and Elliott.[32]

Fig. 2). The strong band at ca. 1640 cm.$^{-1}$ is caused mainly by stretching of the C=O bond and it is also of perpendicular type. However, because it is not entirely a C=O stretching mode the transition moment makes an angle of about 20° with the C=O bond, as first suggested by Fraser and Price[28] and as subsequently verified by examination of crystal

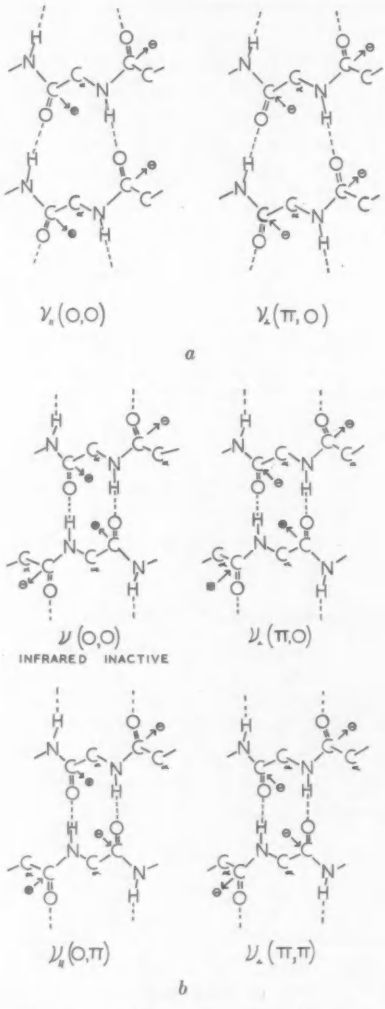


Fig. 3. Vibrational modes (*a*) in parallel hydrogen-bonded polypeptide chains; (*b*) in antiparallel hydrogen-bonded polypeptide chains. From Miyazawa.[27]

layers of model compounds (of known structure) by polarized radiation.[6,24,29] Another strong band, Amide II at ca. 1540 cm.$^{-1}$ is parallel in character, and the motion here involved is largely deformation of the NH bond in the plane of the amide group.

In crystals, and hence in those parts of polymers which are crystalline, only those vibration modes are infrared-active in which the corresponding atoms in all unit cells move in phase. Hence it suffices to consider the

normal modes of the contents of one unit cell. Polyamide chains in crystalline regions usually possess a twofold screw axis, so that there are at least two amide groups in the unit cell. If the chain is a polar one, giving the possibility of an antiparallel arrangement of chains connected by hydrogen bonds, there may be two chains and hence four amide groups in the unit cell. Interactions between amide groups may occur via the hydrogen bond (interchain) or along the polymer chain (intrachain).

Miyazawa[27] has called attention to the importance of these interactions, especially in polypeptides where the same considerations apply. For chains with a twofold screw axis the phase differences between vibrations in the two groups or residues within the one chain are 0 or π. In Miyazawa's treatment, interactions between neighboring groups only are considered. When there is one chain in the unit cells, each mode of the individual groups or residues is split by interaction into two, but with two chains the modes are quadrupled. The motions are shown diagrammatically in Figure 3. The resultant vibration modes are designated by two angles, 0 or π, the first within the parentheses being the phase difference between intrachain groups, the second the phase difference between amide groups connected by a hydrogen bond, e.g., $\nu(0,\pi)$.

In the absence of interaction between identical neighboring groups, but with the modification of frequencies caused by the hydrogen bond, the frequency of a particular mode is designated ν_0. We might expect that randomly coiled polyamide chains in which all hydrogen bonds were formed (in spite of the randomness) would have frequencies approximating to ν_0. Complete absence of interaction would occur if most of the amide groups were *N*-deuterated, the remaining (undeuterated) groups being surrounded by amide groups of different mass, and hence having different frequencies. This method of isolating vibrating systems has been used in several substances.[6,29,29a]

Miyazawa's treatment leads to the following equations for parallel chains.

$$\nu_{\parallel}(0,0) = \nu_0 + D_1 + D_1' \quad (1)$$

$$\nu_{\perp}(\pi,0) = \nu_0 - D_1 + D_1' \quad (2)$$

where D_1 and D_1' are interaction constants for intra- and interchain effects, respectively. For antiparallel chains the equations for the three infrared-active bands are

$$\nu_{\parallel}(0,\pi) = \nu_0 + D_1 - D_1' \quad (3)$$

$$\nu_{\perp}(\pi,0) = \nu_0 - D_1 + D_1' \quad (4)$$

$$\nu_{\perp}(\pi,\pi) = \nu_0 - D_1 - D_1' \quad (5)$$

These components have finite intensity only when there is an appreciable component of the individual transition moment in the appropriate direction. The $\nu_{\perp}(\pi,\pi)$ band, for example, would have zero intensity in a fully

extended, planar polypeptide or polyamide hydrogen-bonded sheet. For polyamides and for polypeptides in the extended or near-extended form, the transition moment of the Amide I band makes a small but appreciable angle with the normal to the chain axis; hence it is to be expected that there will be a strong and, of course, perpendicular band in either a parallel or an antiparallel arrangement. The parallel component should be much weaker.

Considerations such as the above, and also the extension of the theory to α-helical structures have enabled Miyazawa to explain the dependence of the frequency of Amide I and Amide II on chain conformation.[31] Values for the interaction constants D_1 and D_1' have been calculated by Miyazawa and Blout[30] from data on several polymers. It has been pointed out by Bradbury and Elliott[32] that the method of calculation depends on ν_0 remaining constant in different substances. The strong perpendicular Amide I band at 1632 cm.$^{-1}$ and the weak parallel band at 1686 cm.$^{-1}$ in polyglycine[33] are attributed by Miyazawa to $\nu_\perp(\pi,0)$ and $\nu_\parallel(0,\pi)$ of an antiparallel arrangement. Polyglycine is the first member of a homologous series of poly-ω-amino acids with an odd number of CH_2 groups between the amide groups. They are designated nylon 2, 4, etc., and have been examined by Bradbury and Elliott[32] with polarized infrared radiation. Specimens were cast from suitable solvents on films of silver chloride. When the solvent had almost completely evaporated they were rolled out to produce orientation, the solvent being later evaporated.

The structure of nylon 6 has been determined from x-ray diffraction by Holmes, Bunn, and Smith,[34] who have shown that one form is monoclinic with antiparallel chains forming hydrogen-bonded sheets. Although the poly-ω-amino acid series is polymorphic, the even-numbered nylons, when prepared under suitable conditions, are evidently similar in structure to the form studied by Holmes et al., for the x-ray diffraction patterns form a series within which the repeat length changes regularly but the

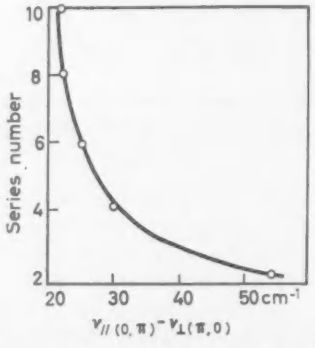


Fig. 4. Separation of Amide I components plotted against polyamide series number. From Bradbury and Elliott.[32]

general appearance is similar throughout. The forms examined by Bradbury and Elliott have infrared spectra in which the structure of Amide I changes in a regular manner throughout the series. These spectra, observed with polarized radiation, are shown in Figure 2. The Amide I band has two components, of which the stronger is perpendicular, the weaker parallel. Except in nylon 2 (polyglycine) the weak component would escape notice were polarized radiation not used, and indeed it does not appear to have been reported before this investigation. It is to be expected that the interaction constant D_1' will be constant throughout the series (interchain interaction) but that D_1 will diminish rapidly with increasing series number. As may be seen in Figure 4, the separation of perpendicular and parallel components diminishes rapidly from nylon 2 to an asymptotic value of 22 cm.$^{-1}$, and since at this point D_1 has become zero, it is easily seen from eqs. (3) and (4) that $D_1' = 11$ cm.$^{-1}$. The interaction constants for the series are given in Table II.

TABLE II

Wave Numbers of Amide I Band Observed in Poly-ω-amino Acids (α,β Form) and Values of D_1 and ν_0[a,b]

Polymer	$\nu_\perp$ $(\pi, 0)$, cm.$^{-1}$	$\nu_\parallel$ $(0, \pi)$, cm.$^{-1}$	ν_0, cm.$^{-1}$	D_1, cm.$^{-1}$
Nylon 2	1632	1686	1659	16
Nylon 4	1640	1670	1655	4
Nylon 6	1642	1667	1654½	1½
Nylon 8	1641	1663	1652	0
Nylon 10	1642	1664	1653	0

[a] Data of Bradbury and Elliott.[32]

[b] The intermolecular constant D_1' is taken as -11 cm.$^{-1}$ throughout.

β-KERATIN

Steam-stretched hair (β-keratin) was shown by Astbury and Street[35] to be composed of nearly extended polypeptide chains, probably hydrogen-bonded into sheets. The x-ray diffraction pattern showed that there were two kinds of chain in these sheets, and this suggests the possibility of an antiparallel chain arrangement. A recent x-ray study has justified and amplified the earlier work, and gives good grounds for believing that antiparallel chains form a considerable part of the structure, though there may be some hydrogen-bonded parallel chains, and there appears to be some randomness in the structure.[36] The infrared evidence has been interpreted as showing that the structure is a parallel one,[30,37] but there is no doubt that a band with parallel dichroism is present at about 1692 cm.$^{-1}$ in steam-stretched hair.[32,38,39] It must be concluded from this that the hydrogen-bonding arrangement is antiparallel, though some parallel hydrogen-bonded chains may be present. The band at 1692 cm.$^{-1}$ may be seen in Figure 5.

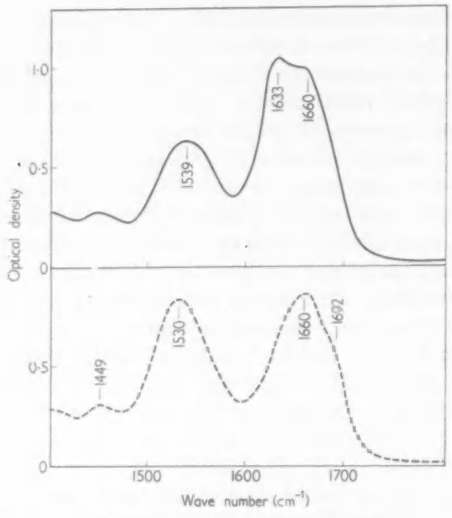


Fig. 5. Infrared spectrum of steam-stretched horse hair: (——) E vector perpendicular to fiber axis; (- - -) E vector parallel to fiber axis. From Bradbury and Elliott.[32]

The molecular structure of feather keratin has not yet been established. The dichroism of the Amide I band is perpendicular,[40] and the chain is probably nearly extended. The frequency of the Amide I band, 1640 cm.$^{-1}$ is higher than in other β-structures.[32] There is no clear indication of a parallel band at ca. 1690 cm.$^{-1}$, but this is not conclusive evidence for the absence of an antiparallel arrangement of hydrogen-bonded chains, for the transition moment of Amide I might be nearly perpendicular to the chain axis, when this band would be of zero intensity. It is perhaps interesting that a random chain direction within the hydrogen-bonded sheet (if such a structure exists in feather keratin) would give a high frequency for Amide I. In such a case, the constant D_1' would be zero, for there would be no regular interaction across the hydrogen bond. With the values for ν_0 and D_1 found for polyglycine (Table II), the frequency of the perpendicular band would be 1643 cm.$^{-1}$, only three wave numbers different from the observed one. The parallel band predicted for such a structure would be 1675 cm.$^{-1}$ and would probably not be detectable.

POLARIZED INFRARED RADIATION AND POLYMER CONFORMATION

Brief reference may be made to some of the early work on fibrous proteins and on synthetic polypeptides, where the use of polarized radiation showed very clearly that the orientation of the amide group with respect to the fiber axis was very different in folded and in extended polypeptides (the nature of the fold was, however, elucidated only with the help of x-ray

diffraction; see, for instance, Pauling and Corey,[41] Bamford, Elliott, and Hanby[16]). More recently, polarization measurements on some synthetic polypeptides have been useful in deciding the conformation of the side chains. Since the orientation which can be obtained in a polymer film is often far from complete, some method of estimating the state of orientation is required before measurements of dichroic ratio can be related to bond directions with respect to molecular axes. Independent methods, such as x-ray diffraction or birefringence, prove to be unsuitable for various reasons, and the best procedure appears to be based on internal measurement of the dichroic ratio for a band (if such exists) the direction of whose transition moment is known. It may happen that the symmetry of the molecule fixes the direction of a transition moment (strictly speaking, this is usually so in polymers, but in most instances bands with different transition moment directions are superposed). An example of a symmetry-controlled direction of transition moment appears in the section on polyamides, and Miyazawa and Blout[30] have used such bands in α-helices to determine the state of orientation of a polymer.

Fraser[25] has proposed a model for an oriented polymer consisting of a fraction f with complete uniaxial orientation, the remainder being unoriented. For a band whose transition moment makes an angle α with the uniaxially oriented molecular axis, the dichroic ratio is

$$D_\pi/D_\sigma = [f \cos^2 \alpha + {}^1/_3 (1 - f)]/[{}^1/_2 f \sin^2 \alpha + {}^1/_3 (1 - f)]$$

It has been shown by Beer[17] that for certain kinds of orientation, including fiber orientation, if a value for f is calculated from this expression using a known value of α and the corresponding measured value of D_π/D_σ, then the correct value of α for a second band may be calculated from its dichroic ratio. This is true if the extinction coefficients of the bands in question are not affected by the physical state of the polymer. If, however, they depend on the chain conformation to different extents for the several bands, then the procedure is not valid.[42] Convenient graphs have been produced giving the relation between D_π/D_σ and f for various values of α.[16,17,19]

The method has been usefully applied to the problem of side-chain conformation in the ω-form of poly-β-benzyl-L-aspartate.[43] A number of bands due to chemical groups in the side chain (chiefly the ester and aromatic groups) were identified, and their dichroic ratios were measured in a well-oriented specimen. The oriented fraction f was determined from one of the amide bands (see original paper for details) and the values of α were calculated. The relation between transition moment direction and bond directions was known approximately from model compounds, or in some cases from symmetry. The information obtained was of considerable use in building models of the structure, even though there is necessarily an ambiguity in the sign of the angle α. The results of the subsequent x-ray work, on which the structure chiefly depends, are in remarkably good agreement with the infrared results. It is worth pointing out that the only discrepancy found was in the case of the deformation mode of a CH_2

group adjacent to an oxygen atom, where possibly the presence of the latter changes the direction of transition moment by some 15°. The angles between the transition moment and helix axis deduced from the measured dichroic ratio and calculated for the model finally adopted are shown in Table III.

INFRARED SPECTRUM OF THE SALTS OF DNA

It is now well established that the genetic material responsible for transmitting hereditary characteristics is deoxyribonucleic acid (DNA). The essential features of the molecular conformation of DNA have been determined from x-ray diffraction studies together with chemical studies and molecular model building.[44–47] It has been found that the molecular conformation of the alkali salts of DNA depends on the nature of the alkali metal and on the water content of the film or fiber and hence on the relative humidity of the air surrounding the specimen. Sodium deoxyribonucleate (NaDNA) can exist in two conformations; the B-form where the

TABLE III
Frequencies, Assignments, and Dichroic Properties of Main Infrared Absorption Bands in Poly-β-benzyl-L-aspartate (ω-Form)[a]

Assignment	Frequency, cm.$^{-1}$	Dichroic ratio $D\pi/D\sigma$	Angle between transition moment and chain axis[b]	
NH stretch	3298	7.0	22°	
Ester C=O	1730	1.5	48°	(50°)
Amide I	1677	3.0	36°	(37°)
	1670			
Amide II	1538	0.20		
	1520			
Aromatic	1501		80°	(81½°)
δCH_2 (adjacent to C=O)	1420	1.3	50½°	(35°)
Ester C—O	1164	0.22	76°	(76½°)
Aromatic C—H out-of-plane	753	0.9	54°	(54°)
Aromatic	698	1.1	54°	(54°)

[a] Data of Bradbury et al.[43]

[b] The figures in the last column (in parentheses) are taken from a model of the ω-helix.

planes of the bases are perpendicular to the helix axis (for humidities greater than 90% R.H.) and the A-form where the planes of the bases are tilted by 20° to make an angle of 70° to the helix axis (humidity around 75% R.H.).[45,46,48] Lithium deoxyribonucleate (LiDNA) can also exist in two forms; the B-form for humidities greater than 66% R.H. and the C-form where the bases are tilted by about 5° for humidities around 44% R.H.[49] Polarized infrared studies of oriented films of the salts of DNA have been made with varying water content of the films.[50–52] Some of these studies have followed the changes between the different conformations

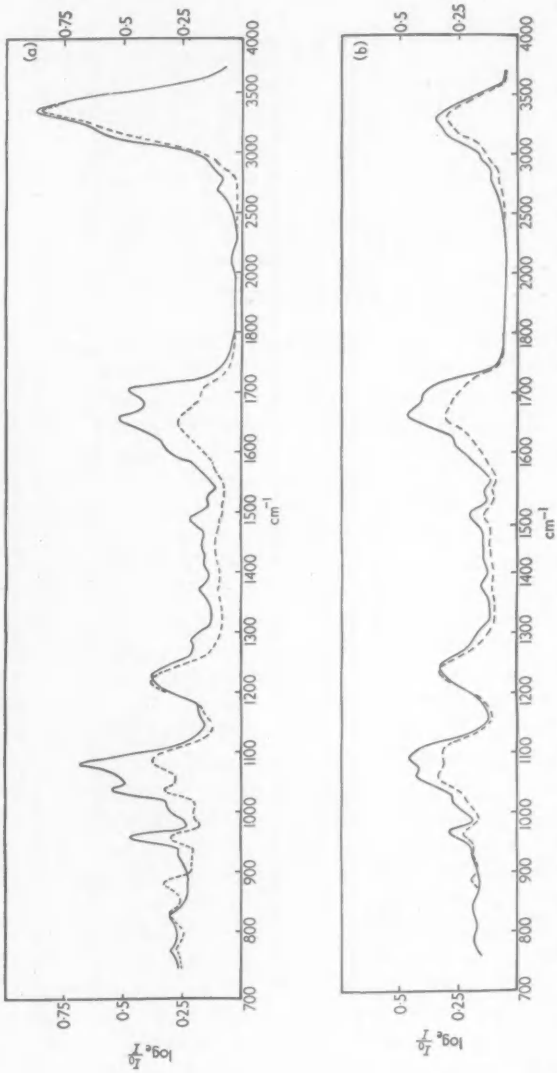


Fig. 6. Infrared spectra of Li-DNA: (*a*) at 86% R.H.; (*b*) at 15% R.H.; (——), (- - -) as in Fig. 5. From Bradbury, Price, and Wilkinson.[51]

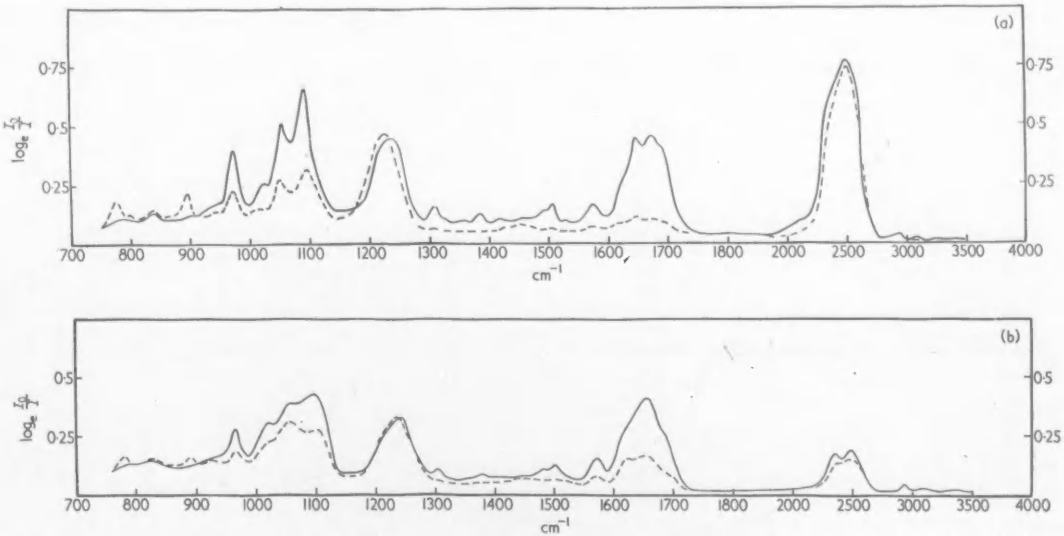


Fig. 7. Infrared spectra of deuterated Li-DNA: (*a*) at 86% R.H. D_2O; (*b*) at 15% R.H. D_2O; (——), (- - -) as in Fig. 5. From Bradbury, Price, and Wilkinson.[51]

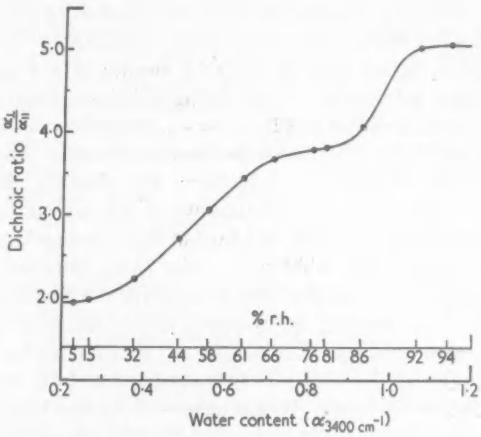


Fig. 8. Plot of the dichroic ratio of in-plane base vibrations for Na-DNA against water content (D_2O) of the specimen. From Bradbury, Price, and Wilkinson.[51]

of DNA and in addition have provided information on the orientation of the phosphate group in the B-form of the DNA molecule.

The B-form of DNA consists of two helical polynucleotide chains coiled around a common axis and held together by hydrogen bonds between specific pairs of bases. The base pairs are stacked one on top of the other separated by the van der Waals distance of 3.4 A. and the angle between adjacent residues is 36°, so that the structure repeats after 10 residues, i.e., every 34 A. along the helix axis. The information deduced from the polarized infrared spectra of LiDNA (Fig. 6) is in complete agreement with the modified structure of Wilkins[49] and co-workers based upon the scheme proposed by Watson and Crick.[44] This is more clearly seen in the polarized spectra of deuterated LiDNA (Fig. 7), where the water band in the important 6 μ region has been replaced by a heavy water band at 1219 cm.$^{-1}$. The strong bands in the 1600–1700 cm.$^{-1}$ region result mainly from stretching vibrations of the double bonds in the bases, and at high humidity (92% R.H.) they show the high perpendicular dichroism expected for in-plane vibrations. As the relative humidity of the surrounding air is reduced, the bands become less dichroic. The polarized spectra of NaDNA are identical with those for LiDNA. A plot of the dichroic ratio ($R = \alpha_\perp/\alpha_\parallel$) against relative humidity for the band at 1672 cm.$^{-1}$ is shown in Figure 8, and two plateaus can be seen, one at humidities greater than 90% R.H. and the other for humidities between 70 and 80% R.H. These plateaus are taken to be an indication of the B- and A-forms of NaDNA. Similar plots, where the plateaus are not so widely separated, have been obtained for LiDNA, indicating the B- and C-forms of LiDNA. Falk, Hartman, and Lord[52] have pointed out that the low dichroisms observed at low humidities indicate a considerable amount of disorder in the packing

of the bases. This is supported by their observation of the hypochromic effect in the band at 2600 A. on drying films of NaDNA. It has also been pointed out[53] that drying films of NaDNA results in a weakening of the specific base–base interaction. The strongly dichroic band at 1708 cm.$^{-1}$ in both NaDNA and LiDNA at 92% shows a hyperchromic effect on drying the specimen which parallels the hypochromic effect of the 2600 A. band observed by Falk, Hartman and Lord.[52] The shift in the 1708 cm.$^{-1}$ band has been attributed to the breakdown of the base pair interactions resulting in a lowering of the force constant of the cytosine C=O.[54]

The strong bands below 1300 cm.$^{-1}$ arise from vibrations of the phosphate-ester chain. For the dry film of LiDNA the bands are broad and ill defined; as the humidity is increased the bands shift slightly in frequency and become sharper, indicating an improvement of crystallinity with water uptake by the film. The strong band at 1245 cm.$^{-1}$ in the dry film is of particular interest. It is nondichroic at low humidities; as the film is hydrated it moves to lower frequencies and splits, the perpendicular component being found at 1228 cm.$^{-1}$ at 92% R.H. while the parallel component is at 1222 cm.$^{-1}$. This band arises from the antisymmetric stretching vibration of the PO_2^- group[50,55] and the splitting indicates the presence of an interaction between the vibrations of adjacent phosphate groups. Both components have the same intensity which shows that the O . . . O line lies close to 55° to the helix axis. The symmetrical stretching vibration of the PO_2^- group is expected at a lower frequency, and Sutherland and Tsuboi[50] originally assigned a band at 1053 cm.$^{-1}$ (at 92% R.H.) to this vibration. More recently, however, Tsuboi[54] quoting work of Kyogoku, Tsuboi, Shimanouchi, and Watanabe,[53] has altered this assignment to the strong band with perpendicular dichroism at 1089 cm.$^{-1}$ (R = 2.0:1). This would indicate that the transition moment for the symmetrical stretching vibration of the PO_2^- group, which bisects the OPO angle, lies close to 67° to the helix axis. Sutherland and Tsuboi[50] have pointed out that in the original structure proposed by Crick and Watson[44] the orientation of the phosphate group would give dichroisms quite different from those observed. The orientation of the PO_2^- group in the modified structure[46,47] has been changed to fit in with the results from polarized infrared studies.

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Discussion

S. Krimm (*University of Michigan, Ann Arbor, Michigan, U.S.A.*): I want to ask Dr. Elliott and perhaps Dr. Miyazawa a question. This refers to the interaction theory of explaining some of the frequency shifts in terms of protein conformations. It seems to me that the outlines and the general direction of the theory proposed by Dr. Miyazawa are quite correct. There seems to be also at the moment a little problem about how to assign unperturbed frequencies and interaction constants, how many interaction constants might be involved, is the D_1 in fact constant as one goes from one series to another, and so on. I should like to ask first a very short question of Dr. Elliott. Does one know in fact from the crystal structure of these various nylons that the hydrogen bonding distance is constant throughout the series that you were looking at?

A. Elliott: The unit cells proposed for these polymers are similar (except for the length of the chain axis repeat), but accurate values of the hydrogen bond length do not appear to have been published except for nylon 6.

T. Miyazawa (*Osaka University, Japan*): We know that the NH stretching frequencies of the peptide group are sensitive and vary with the strength of the hydrogen bonds We might then look at the bands observed at 3300 cm.$^{-1}$. But, in that case, we again are disturbed somewhat by the interaction with the first overtone of the amide II vibration, so perhaps one should look at the hydrogen bond distance as Dr. Krimm suggests.

S. Krimm: The other question has to do with something which Dr. Elliott did not bring up directly but is involved, I think, in all the discussions of protein spectra. My question has to do with the assignment of the Amide II unperturbed frequency ν_0. I think that both Dr. Miyazawa and Dr. Elliott have assigned this frequency from studies of partially deuterated polypeptides on the assumption that when a good proportion of the peptide groups are deuterated the remaining undeuterated peptide groups will not experience the interaction. Therefore one would be able to measure the interaction parameter. I wonder if this is correct in the following sense: ν_0 refers to a completely unperturbed mode which corresponds to an unordered structure in which there are no interactions. While it is true that in the deuterated or partially deuterated material there may not be the D_1 type of interaction, the peptide group finds itself in a rather different environment. As one melts nylon 66 the Amide I frequency, at about 1640 cm.$^{-1}$ moves over to 1660 cm.$^{-1}$. Such a value is rather close to the ν_0 value that I think most of us find. At the same time the amide II band moves over to 1520 cm.$^{-1}$ which does not correspond to the ν_0 value of 1540 cm.$^{-1}$ which you both suggested. I wonder if you would care to comment on that.

A. Elliott: In answer to Dr. Krimm I would have thought that in the case of nylon raised to a high temperature, one had a good reason for thinking that perhaps the length of the hydrogen bonds was not the same in all the molecules as it was at the lower temperature. You have done something fairly drastic to the structure and possibly the change in the frequency of the amide I band means that you have weakened hydrogen bonds as well as a disordered structure. If you have hydrogen bonds which are of different length this will affect the frequency of Amide II. Is this not a likely thing?

S. Krimm: This is, in fact, what does happen because the N—H stretching mode goes to higher frequency, indicating a much weaker hydrogen bond. But the point is that in that case we have a situation where both D_1' and D_1 go effectively to zero. The remaining band that we see is then presumably ν_0 At least it corresponds in frequency to it. Therefore I'm asking whether one shouldn't similarly infer that all the interaction parameters for the Amide II band have also gone to zero essentially. Therefore what is left is the unperturbed ν_0 for Amide II.

A. Elliott: I would like to hear what Dr. Miyazawa has to say about this. My understanding of the ν_0 term is that the polymer is supposed to be subject to the same constraint of the hydrogen bond as it is in the crystal. I think that if you disturb the strength of the hydrogen bond then it is a different ν_0 from the one that I've been thinking of.

T. Miyazawa: A few years ago when we proposed the interaction theory for the Amide I and II vibrations, we were not too much worried about variations of 5 or 10 cm.$^{-1}$. The theory, as it was proposed at that time, was crude in many respects. We assumed that is fairly constant in various molecules. On the contrary, particularly for the case of the Amide II band, as studied by Dr. Elliott, ν_0 seems to vary from molecule to molecule. When we proposed this theory I perceived that the vibrational interaction among amide groups could have been averaged out and we did not expect too much interaction to show up in random forms or random conformers. Many structures are possible in the so called random coiled form. We might have short segments of the antiparallel chain arrangement of the parallel chain arrangement or, in some cases, the α-helical segments, and if we think of the intensity of the various modes, one might become involved in such a complicated situation that it become impossible to proceed any further in the interpretation. I would like to add a remark on the incompletely deuterated species. For those compounds for which we observe the amide II band due to the undeuterated CO—NH group that CO—NH group, I presume, is in much the same environment as the undeuterated polypeptides and I think that this Amide II frequency is pretty close to the unperturbed ν_0 frequency.

A. Elliott: This would have been my opinion too. I would have thought that this was a fairly good approximation to ν_0 but I'm not sure that Dr. Krimm is convinced of it.

S. Krimm: I don't want to take up too much time with this point, but there are several things which disturb me. For example, in a deuterated species of the α-helix, one knows that the repeat distance along the axis has changed slightly. In fact it has increased in a deuterated specimen. This means that the inter group constant D_1, or at least the hydrogen bonding situation, would not be identical to the undeuterated case. As a matter of fact from the very beginning I've been worried about the assumption (which I think we have all had to make because of paucity of data) that D_1' in the α-helix be the same as D_1' in the extended chain structures. And then for the α-helix one takes the two observed frequencies, assumes D_1' the same, computes D_1 for one of them and shows that it gives a consistant explanation of the second. This point bothers me a little. In particular if one looks only at the experimental data for nylon 66 in going from the solid state to the melt, the residual frequency for Amide I is very close to ν_0 that is calculated by this scheme. I wonder why one shouldn't also think that the residual frequency for Amide II (which is closer to 1520 cm.$^{-1}$ than to the 1540 cm.$^{-1}$) is the unperturbed value. Incidentally, I want to mention that for nylon 66 in going from the solid state to the melt the change in N—H frequency is quite small. The N—H stretching frequency of the melt nylon is only 15 cm.$^{-1}$ higher than that of the crystalline substance. I do not think that any loss of hydrogen bonding occurs, but presumably an unordering of the structure takes place.

T. Miyazawa: I would like to point out that the so-called N—H stretching frequencies are subject to Fermi resonance with the first overtone of the Amide II vibration.

S. Califano (*Universita di Napoli, Naples, Italy*): I would like to ask Dr. Miyazawa how large is the coupling among the vibrations of C—N, N—H, and C—O in the Amide II band.

T. Miyazawa: The potential energy of the Amide II vibration is associated 10% with the C—O stretching, 50% for the N—H bending, and 40% with the C—N stretching modes. The amplitude ratio is C—N: C—O = 4:1.

S. Califano: I then suggest that the shift which has been discussed may be originated from a change of the mixing between the various internal coordinates along with the change of the strength of the hydrogen bond.

T. Miyazawa: Certainly the mixing should vary with the strength of the hydrogen bond. But if you decrease the strength of the hydrogen bond you will decrease the the bond order of the C—N bond and increase the C=O bond order. I should like to add another comment. I agree with Dr. Elliott and Dr. Krimm in saying that the polarized infrared measurement is extremely useful for the structural studies of polymers. However I would like to remind you that in this kind of study one can be led to some incorrect structure as in the case of isotactic polypropylene and its deuteroderivatives where calculated intensity ratios of the perpendicular to the parallel components of the CH_2 bending modes are not completely in accord with the measured values.

A. Elliott: I certainly agree with Dr. Miyazawa that one can be misled by assuming that one knows the directions of transition moments and in calculating structures from them. There are other examples too of course. I do not know whether the controversy on poly(ethylene terephthalate) has been altogether resolved, where the dichroism of the CH_2 band was not that expected from the structures determined by Bunn. These things do happen and one has to be on the lookout for them. I certainly think that the dichroic ratio is not a very quantitative and reliable tool unless one checks in a number of points.

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Theory of Normal Vibrations of Helical Polymers and Vibrational Assignment of the Infrared Spectra of Isotactic Polypropylene

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Isotactic polypropylene $[-CH_2-CH(CH_3)-]_n$ is structurally typical of a large number of isotactic polymers. Detailed infrared studies of isotactic polypropylene will provide basic knowledge necessary for vibrational analyses and structure studies of other isotactic polymers. The infrared spectra of isotactic polypropylene and its deuterated derivatives have been measured and empirical vibrational assignments have been made.[1–8] The effect of isotopic substitutions of CH, CH_2, and CH_3 groups upon the infrared spectra have been found to be quite complicated. Except for the bands arising from the CH_3 symmetric or asymmetric deformation vibrations or for the bands due to the CH_2 bending vibrations, all the infrared bands in the region 1500–600 cm.$^{-1}$ have been found to shift more or less upon the deuterium substitution of any of the CH, CH_2, and CH_3 groups. Therefore, from empirical analyses of observed isotope effects, all these bands have been considered to be due to hybridized modes of the CH, CH_2, and CH_3 groups. Accordingly, the normal coordinate analyses are indispensable in elucidating the nature of the infrared bands observed for polypropylene and deuterated derivatives.

GENERAL METHOD FOR TREATING THE NORMAL VIBRATIONS OF HELICAL POLYMERS

The normal vibrations of infinite helical polymeric chains may be specified by the phase difference δ between the vibrational displacements of the corresponding atoms in adjacent units. The number of normal vibrations for any given phase difference may be expressed in terms of the number p of atoms per repeating unit. There are $3p - 2$ A vibrations with the phase difference of $\delta = 0$; $3p - 1$ pairs of degenerate $E(\delta)$ vibrations for the phase difference of $\delta = \theta$; and $3p$ pairs of degenerate $E(\delta)$ vibrations for the phase differences $\delta \neq \theta$, where the angle θ is the angle of rotation about the helix axis on passing from an atom to the corresponding atom of the adjacent unit. The A vibrations give rise to parallel infrared bands, whereas the $E(\theta)$ vibrations give rise to perpendicular bands. All the other vibrations of infinite helical chains are not active in the infrared absorption.[9]

A general method for treating the normal vibrations of infinite helical polymers by the GF matrix method[10] was first worked out by Higgs.[9] The infinite G (or F) matrix may be expressed in terms of the internal coordinate vectors, R_m denoting the vector associated with the mth repeating unit:

$$\begin{array}{cccccccc}
R_{m-s}^{\dagger} & & R_{m-2}^{\dagger} & R_{m-1}^{\dagger} & R_m^{\dagger} & R_{m+1}^{\dagger} & R_{m+2}^{\dagger} & \cdots\ R_{m+s}^{\dagger} \\
R_{n-1}\ \cdots\ G^{s-1} & & \cdots\ G^{1} & G^{0} & & {}^{1\dagger} & G^{2\dagger} & G^{3\dagger}\ \cdots\ G^{s+1\dagger} \\
R_m\ \cdots\ G^{s} & & \cdots\ G^{2} & G^{1} & G_{\dagger}^{0} & G^{1\dagger} & G^{2\dagger} & \cdots\ G^{s\dagger} \\
R_{m+1}\ \cdots\ G^{s+1} & & \cdots\ G^{3} & G^{2} & G^{1} & G^{0} & G^{1\dagger} & \cdots\ G^{s-1\dagger}
\end{array}$$

The infinite G (or F) matrix may be factored into the set of matrices $G(\delta)$ [or $F(\delta)$] corresponding to the phase difference of δ. The internal symmetry coordinate vectors for the phase difference δ are given by eqs. (1) and (2):

$$S^{+}(\delta) = N^{-1/2} \sum_m R_m \exp\{im\,\delta\} \tag{1}$$

$$S^{-}(\delta) = N^{-1/2} \sum_m R_m \exp\{-im\,\delta\} \tag{2}$$

where $N^{-1/2}$ is the normalization factor. The G matrix for the phase difference δ is now factored into the $G^{+}(\delta)$ matrix and the $G^{-}(\delta)$ matrix, each associated with the symmetry coordinate vectors, $S^{+}(\delta)$ and $S^{-}(\delta)$, respectively.

$$G^{+}(\delta) = G^{0} + \sum_s (G^{s} + G^{s\dagger}) \cos s\delta + i \sum_s (G^{s} - G^{s\dagger}) \sin s\delta \tag{3}$$

$$G^{-}(\delta) = G^{0} + \sum_s (G^{s} + G^{s\dagger}) \cos s\delta - i \sum_s (G^{s} - G^{s\dagger}) \sin s\delta \tag{4}$$

The order of the $G^{+}(\delta)$ or the $G^{-}(\delta)$ matrix is equal to the number n of internal coordinates per repeating unit. For the A vibrations with a phase difference of $\delta = 0$, the $G(0)$ matrix is given by eq. (5):

$$G(0) = G^{0} + \sum_s (G^{s} + G^{s\dagger}) \tag{5}$$

The potential energy matrix, $F^{+}(\delta)$ or $F^{-}(\delta)$ are expressed in the same form as the $G^{+}(\delta)$ or $G^{-}(\delta)$ matrix. The elements of the $G^{+}(\delta)$ or $G^{-}(\delta)$ matrices as given by eqs. (3) and (4) are complex numbers. However, it is more practical to deal with real G and F matrices, and then the GF matrix may be transformed into symmetrical form, and may be diagonalized to yield the normal frequencies and normal modes.[11,12]

The real internal symmetry coordinate vectors, $S^{c}(\delta)$ and $S^{s}(\delta)$, for the phase difference of δ are obtained from $S^{+}(\delta)$ and $S^{-}(\delta)$,

$$S^{c}(\delta) = 2^{-1/2}\,[S^{+}(\delta) + S^{-}(\delta)] = (2/N)^{1/2} \sum_m R_m \cos m\delta \tag{6}$$

$$S^{s}(\delta) = -2^{-1/2}\,i[S^{+}(\delta) - S^{-}(\delta)] = (2/N)^{1/2} \sum_m R_m \sin m\delta \tag{7}$$

Then the $\boldsymbol{G}(\delta)$ matrix for the phase difference δ may be expressed in terms of these real symmetry coordinate vectors,

$$\boldsymbol{G}(\delta) = \begin{bmatrix} \boldsymbol{G}_1(\delta) & -\boldsymbol{G}_2(\delta) \\ \boldsymbol{G}_2(\delta) & \boldsymbol{G}_1(\delta) \end{bmatrix} \tag{8}$$

where

$$\boldsymbol{G}_1(\delta) = \boldsymbol{G}^0 + \sum_s (\boldsymbol{G}^s + \boldsymbol{G}^{s\dagger}) \cos s\delta \tag{9}$$

$$\boldsymbol{G}_2(\delta) = \sum_s (\boldsymbol{G}^s - \boldsymbol{G}^{s\dagger}) \sin s\delta \tag{10}$$

The order of the real $\boldsymbol{G}(\delta)$ matrix as given by eq. (8) is twice the number (n) of the coordinates per repeating unit; however, the number of the independent elements is equal to n^2, since the number of the independent elements of the $\boldsymbol{G}_1(\delta)$ matrix (symmetric) and the $\boldsymbol{G}_2(\delta)$ matrix (skewsymmetric) is equal to $n(n+1)/2$ and $n(n-1)/2$, respectively. The real $\boldsymbol{F}(\delta)$ matrix is expressed in the same form as eq. (8).

A general method (and also computation procedures) has been described previously[12] for calculating the normal frequencies and normal modes from the $\boldsymbol{G}(\delta)$ and $\boldsymbol{F}(\delta)$ matrices as given by eq. (8). The symmetry coordinate vectors may be derived as

$$\boldsymbol{S}^c(\delta) = \boldsymbol{L}_\alpha(\delta)\boldsymbol{Q}_a(\delta) - \boldsymbol{L}_\beta(\delta)\boldsymbol{Q}_b(\delta) \tag{11}$$

$$\boldsymbol{S}^s(\delta) = \boldsymbol{L}_\beta(\delta)\boldsymbol{Q}_a(\delta) + \boldsymbol{L}_\alpha(\delta)\boldsymbol{Q}_b(\delta) \tag{12}$$

where $\boldsymbol{Q}_a$ and $\boldsymbol{Q}_b$ are the degenerate pair of the normal coordinates. On the other hand, from eqs. (6) and (7), the internal coordinate vector, $\boldsymbol{R}_m$, of the mth repeating unit is given as

$$\boldsymbol{R}_m = (2/N)^{1/2} \sum_\delta [\boldsymbol{S}^c(\delta) \cos m\delta + \boldsymbol{S}^s(\delta) \sin m\delta] \tag{13}$$

Therefore, when the pth degenerate vibration with phase difference δ is excited, the ith internal coordinate of the mth unit is derived to be

$$\begin{aligned} R_{im} &= (2/N)^{1/2} \{ [(L_\alpha)_{ip} \cos m\delta + (L_\beta)_{ip} \sin m\delta] Q_{pa}(\delta) \\ &\qquad + [-(L_\beta)_{ip} \cos m\delta + (L_\alpha)_{ip} \sin m\delta] Q_{pb}(\delta) \} \\ &= (2/N)^{1/2} L_{ip}(\delta) \{ Q_{pa}(\delta) \cos[(m\delta + \epsilon_{ip}(\delta)] \\ &\qquad + Q_{pb}(\delta) \sin[m\delta + \epsilon_{ip}(\delta)] \} \end{aligned} \tag{14}$$

where

$$L_{ip} = [(L_\alpha)_{ip}^2 + (L_\beta)_{ip}^2]^{1/2} \tag{15}$$

$$\epsilon_{ip} = \tan^{-1} [-(L_\beta)_{ip}/(L_\alpha)_{ip}] \tag{16}$$

Thus when a degenerate vibration is excited, the ith internal coordinate of the mth unit is given by the amplitude factor $L_{ip}(\delta)$ and the phase angle of $[m\delta + \epsilon_{ip}(\delta)]$. The phase difference between the ith coordinate of the mth unit and the ith coordinate of the mth unit is $[(m' - m)\delta + (\epsilon_{i'p} - \epsilon_{ip})]$. (For the A vibrations with phase difference of $\epsilon = 0$, all the phase

angles are equal to zero and the normal modes are given by the amplitude L_{ip} alone.)

The potential energy distribution (PED) and the kinetic energy distribution (KED) have been found to be useful for discussions on the nature of the normal vibration in question.[13,14] For the pth normal vibration (a or b) of an infinite helical polymer molecule, the potential energy associated with the ith and jth coordinates is given as

$$V_{ij} = \sum_{s} \sum_{m} F_{i,j}{}^{s} R_{i,m} R_{j,m+s} /2 \tag{17}$$

Substituting eq. (14) into eq. (17) and making summations over m, we have

$$V_{ij} = \sum_{s} L_{ip} L_{jp} G_{i,j}{}^{s} \cos [s\delta + (\epsilon_{jp} - \epsilon_{ip})] Q_p{}^2/2 \tag{18}$$

Now, since the total potential energy of the pth vibration is equal to $(4\pi^2 c^2 \nu_p) Q_p{}^2/2$, the fraction of the potential energy associated both with the ith and jth coordinates is derived to be

$$(\mathrm{PED}_p)_{i,j} = L_{ip} L_{jp} \sum_{s} F_{i,j}{}^{s} \cos[s\delta + (\epsilon_{jp} - \epsilon_{ip})]/4\pi^2 c^2 \nu_p \tag{19}$$

Similarly, the fraction of the kinetic energy associated both with the ith and jth coordinates, $(\mathrm{KED}_p)_{i,j}$, may be obtained by replacing $F_{i,j}{}^{s}/4\pi^2 c^2 \nu_p{}^2$ of eq. (19) with $(G^{-1})_{i,j}{}^{s}$.

It may be recalled that, for helical polymers having twofold axes (perpendicular to the helix axis) the $\boldsymbol{G}(\delta)$ matrix for degenerate vibrations may be factored into a matrix associated with the symmetry coordinate vector $\boldsymbol{S}_A(\delta)$ and the identical matrix associated with the symmetry coordinate vector $\boldsymbol{S}_B(\delta)$. The former vector is symmetric with respect to the twofold axis passing through the zeroth atom whereas the latter vector is antisymmetric with respect to this axis.[15] Thus, the $\boldsymbol{G}(\delta)$ matrix can be factored because of the presence of the twofold axes other than the helix axis. On the other hand the helical chain of isotactic polypropylene does not have any symmetry element other than the helix axis, and the $\boldsymbol{G}(\delta)$ matrix cannot be similarly factored.

FAR INFRARED SPECTRA OF ISOTACTIC POLYPROPYLENE

The infrared spectra of highly crystalline films of isotactic polypropylene have been measured in the region 600–280 cm.$^{-1}$ with a Perkin-Elmer Model 221 spectrometer (potassium bromide optics for the region 900–400 cm.$^{-1}$ and cesium bromide optics for the region 600–280 cm.$^{-1}$)[12] (Fig. 1). Isotactic polypropylene sheets (2 mm. in thickness) were prepared by hot pressing of Moplen powder (Mitsubishi Petrochemical Co. Ltd.) at 190°C. and were subsequently uniaxially oriented. For dichroic measurements, a pair of polyethylene polarizers were used, each consisting of ten polyethylene sheets 0.02 mm. in thickness.

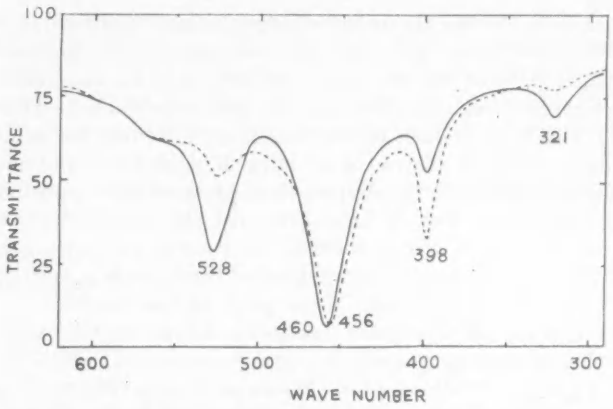


Fig. 1. Polarized infrared spectra of oriented crystalline film (2 mm. thick) of isotactic polypropylene: (——) electric vector perpendicular and (- - -) electric vector parallel to the direction of orientation. Data of Miyazawa et al.[12]

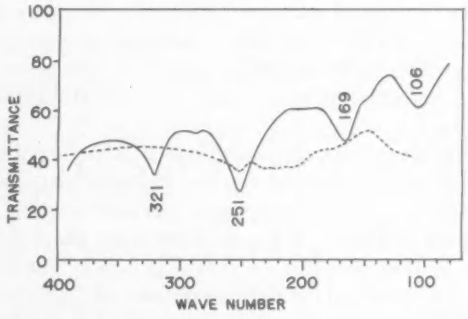


Fig. 2. Far infrared spectra of isotactic (—) and atactic (- - -) polypropylene. Data of Miyazawa et. al.[16]

The polarized far infrared spectra (400–80 cm.$^{-1}$)[16] have also been measured with a Perkin-Elmer Model 201C far infrared spectrometer. The observed frequencies (and dichroism) are listed in Table III. The far infrared spectrum has been measured for atactic sample which has been synthesized at 70°C. in *n*-heptane solution with $AlCl_3$ as a catalyst. The atactic sample, however, does not exhibit well-defined absorption bands in the far infrared region (Fig. 2).

NORMAL COORDINATE TREATMENT OF ISOTACTIC POLYPROPYLENE

The crystal structure of isotactic polypropylene (modification I) was studied by Natta et al.[17] There are four chains passing through the unit cell, and in principle, the interchain interactions should be taken into

consideration in treating the optically active normal vibrations. However, no spectral differences have been observed between the infrared bands (above 750 cm.$^{-1}$) of the two modifications (I and II) of isotactic polypropylene, even though the packing of the molecular chains is different for I and II.[18] The interchain interactions may, therefore, be ignored; at least in the vibrational analysis of the infrared bands above 750 cm.$^{-1}$.

A single chain of isotactic polypropylene contains three repeating units, $-CH_2-CH(CH_3)-$, and one helical turn per fiber identity distance, and accordingly $\theta = 2\pi/3$. Since there are nine atoms per repeating unit, a total of 25 A vibrations give rise to parallel bands while a total of 26 degenerate $E(2\pi/3)$ vibrations give rise to perpendicular bands.

In our first normal coordinate treatment, the normal vibrations of isotactic polypropylene were calculated with the neglect of the C—H stretching or the internal-rotation modes. Subsequently the "effective" potential constants of isotactic polypropylene were calculated by the method of least squares[19] from the observed frequencies of $[-CH_2-CH(CH_3)-]_n$, $[-CH_2-CD(CH_3)-]_n$, $[-CD_2-CH(CH_3)-]_n$, and $[-CH_2-CH(CD_3)-]_n$ (in the region 1500–600 cm.$^{-1}$) and the nature of the infrared bands was discussed with reference to the normal modes and the potential energy distributions.[20] The low frequency normal vibrations of isotactic polypropylene were also calculated where the internal-rotation potential terms were taken into account and the potential constants were transferred from molecules with similar structures.[16]

In our recent study, the normal vibrations of isotactic polypropylene and deuterated derivatives are calculated where the high frequency CH(or CD) stretching modes and the low frequency internal rotation modes are all taken into account. The C—C bonds of the main chain are either nearly parallel or nearly perpendicular to the helix axis. The former class of bonds is denoted as axial and the latter as equatorial C—C bonds (analogous to the bonds of the cyclohexane ring). The internal rotation angle about the axial C—C bond is taken as 60° (*gauche*) and the internal rotation angle about the equatorial C—C bonds as 180° (*trans*). The bond between a carbon atom of the chain and a methyl carbon atom is denoted as a C—M bond. The C—M bond is assumed to have the staggered conformation.

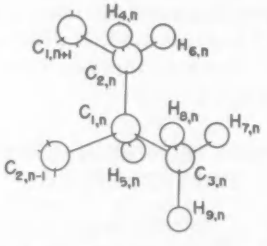


Fig. 3. Numbering of the carbon and hydrogen atoms of the isotactic polypropylene chain (right-handed helix).

For the calculation of the inverse kinetic energy matrix ($\boldsymbol{G}$), the bond lengths C—C = 1.54 A. and C—H = 1.09 A. and the tetrahedral bond angles were used. The $\boldsymbol{G}$ matrix elements associated with the internal rotation modes about the axial and equatorial C—C bonds and the C-methyl bonds were calculated by the general formulae as reported previously.[21]

The internal coordinates (or local symmetry coordinate) vector, $\boldsymbol{R}_m$, of the mth repeating unit are,

$$\begin{bmatrix} R_{1,m}(\text{CH bend}^{ax}) \\ R_{2,m}(\text{CH bend}^{eq}) \\ R_{3,m}(\delta^s) \\ R_{4,m}(\delta^a \text{ ax}) \\ R_{5,m}(\delta^a \text{ eq}) \end{bmatrix} = \begin{bmatrix} 0 & 1/6^{1/2} & 0 & 1/6^{1/2} & 0 & -2/6^{1/2} \\ 0 & -1/2^{1/2} & 0 & 1/2^{1/2} & 0 & 0 \\ 1/6^{1/2} & -1/6^{1/2} & 1/6^{1/2} & -1/6^{1/2} & 1/6^{1/2} & -1/6^{1/2} \\ -2/6^{1/2} & 0 & 1/6^{1/2} & 0 & 1/6^{1/2} & 0 \\ 0 & 0 & -1/2^{1/2} & 0 & 1/2^{1/2} & 0 \end{bmatrix} \phi(\text{CH})_m \tag{20}$$

$$R_{6,m}[\nu(\text{CH})] = \Delta r(1,m;5,m) \tag{21}$$

$$R_{7,m}(r_{\text{CM}}) = \Delta r(1,m;3,m) \tag{22}$$

$$\begin{bmatrix} R_{8,m}[\nu_s(\text{CH}_3)] \\ R_{9,m}[\nu_a'(\text{CH}_3)] \\ R_{10,m}[\nu_a''(\text{CH}_3)] \end{bmatrix} = \begin{bmatrix} 1/3^{1/2} & 1/3^{1/2} & 1/3^{1/2} \\ -1/6^{1/2} & 2/6^{1/2} & -1/6^{1/2} \\ 1/2^{1/2} & 0 & -1/2^{1/2} \end{bmatrix} \begin{bmatrix} \Delta r(3,m;7,m) \\ \Delta r(3,m;8,m) \\ \Delta r(3,m;9,m) \end{bmatrix} \tag{23}$$

$$\begin{bmatrix} R_{11,m}(\text{CH}_3\ \delta_s^{ax}) \\ R_{12,m}(\text{CH}_3\ \delta_a^{eq}) \\ R_{13,m}(\text{CH}_3\ \delta_s) \\ R_{14,m}(\text{CH}_3\ \text{rock}^{ax}) \\ R_{15,m}(\text{CH}_3\ \text{rock}^{eq}) \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 1/6^{1/2} & 1/6^{1/2} & -2/6^{1/2} \\ 0 & 0 & 0 & 1/2^{1/2} & -1/2^{1/2} & 0 \\ -1/6^{1/2} & -1/6^{1/2} & -1/6^{1/2} & 1/6^{1/2} & 1/6^{1/2} & 1/6^{1/2} \\ -1/6^{1/2} & -1/6^{1/2} & 2/6^{1/2} & 0 & 0 & 0 \\ -1/2^{1/2} & 1/2^{1/2} & 0 & 0 & 0 & 0 \end{bmatrix} \phi(\text{CH}_3)_m \tag{24}$$

$$R_{16,m}(r_{\text{CC}}^{ax}) = \Delta r(1,m;2,m) \tag{25}$$

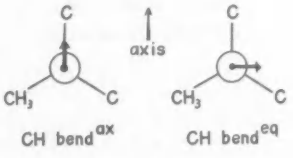


Fig. 4. Axial and equatorial CH bending modes.

$$\begin{bmatrix} R_{17,m}[\nu_s(CH_2)] \\ R_{18,m}[\nu_a(CH_2)] \end{bmatrix} = \begin{bmatrix} 1/2^{1/2} & 1/2^{1/2} \\ -1/2^{1/2} & 1/2^{1/2} \end{bmatrix} \begin{bmatrix} \Delta r(2,m;4,m) \\ \Delta r(2,m;6,m) \end{bmatrix} \tag{26}$$

$$\begin{bmatrix} R_{19,m}(\delta) \\ R_{20,m}(CH_2\ \text{bend}) \\ R_{21,m}(CH_2\ \text{wag}) \\ R_{22,m}(CH_2\ \text{twist}) \\ R_{23,m}(CH_2\ \text{rock}) \end{bmatrix}$$

$$= \begin{bmatrix} 1/30^{1/2} & 1/30^{1/2} & -5/30^{1/2} & 1/30^{1/2} & 1/30^{1/2} & 1/30^{1/2} \\ 1/20^{1/2} & 1/20^{1/2} & 0 & -4/20^{1/2} & 1/20^{1/2} & 1/20^{1/2} \\ 1/2 & 1/2 & 0 & 0 & -1/2 & -1/2 \\ -1/2 & 1/2 & 0 & 0 & 1/2 & -1/2 \\ 1/2 & -1/2 & 0 & 0 & 1/2 & -1/2 \end{bmatrix} \phi(CH_2)_m \tag{27}$$

$$R_{24,m}(r_{CC}^{eq}) = \Delta r(2,m;1,m+1) \tag{28}$$

$$R_{25,m}(t_{CM}) = \Delta t(1,m;3,m) \tag{29}$$

$$R_{26,m}(t_{CC}^{ax}) = \Delta t(1,m;2,m) \tag{30}$$

$$R_{27,m}(t_{CC}^{eq}) = \Delta t(2,m;1,m+1) \tag{31}$$

where Δr's and Δt's are the stretching coordinates and internal rotation coordinates, respectively, for which the numbering of carbon and hydrogen atoms are shown in Figure 3. The elements of the vector $\phi(CH)_m$ in eq. (20) are, $\Delta\phi(2,m-1;1,m;3,m)$, $\Delta\phi(2,m-1;1,m;5,m)$, $\Delta\phi(2,m-1;1,m;2,m)$, $\Delta\phi(3,m;1,m;5,m)$, $\Delta\phi(3,m;1,m;2,m)$, and $\Delta\phi(5,m;1,m;2,m)$. The elements of the vector $\phi(CH_3)_m$ in eq. (24) are $\Delta\phi(1,m;3,m;7,m)$, $\Delta\phi(1,m;3,m;8,m)$, $\Delta\phi(1,m;3,m;9,m)$, $\Delta\phi(8,m;3,m;9,m)$, $\Delta\phi(9,m;3,m;7,m)$, and $\Delta\phi(7,m;3,m;8,m)$. The elements of the vector $\phi(CH_2)_m$ in eq. (27) are, $\Delta\phi(1,m;2,m;4,m)$, $\Delta\phi(1,m;2,m;6,m)$, $\Delta\phi(1,m;2,m;1,m+1)$, $\Delta\phi(4,m;2,m;6,m)$, $\Delta\phi(4,m;2,m;1,m+1)$, and $\Delta\phi(6,m;2,m;1,m+1)$, where $\Delta\phi$'s are the angle bending coordinates for which the numbering of the atoms are shown in Figure 3.

For the CH group of polypropylene, there are two CH bending modes. The bending mode in the axial direction (CH bend^{ax}) and the bending mode in the equatorial direction (CH bend^{eq}) are shown in Figure 4. For the CH_3 group, there are two asymmetric deformation modes and two rocking modes. The asymmetric deformation modes in the axial direction (CH_3 δ_a^{ax}) and in the equatorial direction (CH_3 δ_a^{eq}) and the rocking modes in the axial direction (CH_2 rock^{ax}) and in the equatorial direction (CH_3 rock^{eq}) are shown in Figure 5.

In deriving the potential energy matrix ($\boldsymbol{F}$), the modified Urey-Bradley force field[22] was supplemented with the internal rotation potential terms.[21]

$$V(\text{internal-rotation}) = {}^1/_2 \sum_m \{ Y(\text{CH—CH}_3)\ [\Delta t(1,m;3,m)]^2 + Y(\text{CH—CH}_2)\ [\Delta t(1,m;2,m)]^2 + Y(\text{CH—CH}_2)\ [\Delta t(2,m;1,m+1)]^2 \} \tag{32}$$

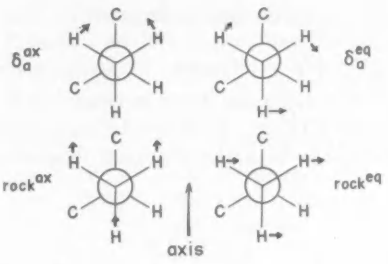


Fig. 5. Axial and equatorial CH_3 asymmetric deformation modes and rocking modes.

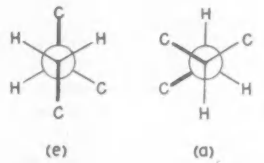


Fig. 6. Spatial arrangement of the carbon and hydrogen atoms of the isotactic polypropylene chain (right-handed helix): (*e*) as viewed along the equatorial C—C bond; (*a*) as viewed along the axial C-C bond. Main chain C-C bonds are drawn with heavy lines.

The *trans*-coupling potential[23–25] for pairs of C—C—H angles in the *trans* arrangement, the *gauche*-coupling potential[24] for pairs of C—C—H angles in the *gauche* arrangement, the l(C—C—H) angle-interaction potential[23,24,26] and the p(C—H) bond interaction potential terms[27] were added as correction terms to the Urey-Bradley force field.[28a]

The repulsion constants, F(H—C—H) and F(H—C—C), were transferred from the ethane molecule as treated recently by Shimanouchi and Takahashi.[27] The initial set of all the other potential constants were transferred from the previous study[20] and were then adjusted by the method of least squares.[19] The fundamental frequencies of $[—CH_2—CH(CH_3)—]_n$, $[—CH_2—CD(CH_3)—]_n$, $[—CD_2—CH(CH_3)—]_n$, and $[—CH_2—CH(CD_3)—]_n$ observed by Peraldo and Farina[1] in the region above 650 cm.$^{-1}$ and also the far infrared frequencies of $[—CH_2—CH(CH_3)—]_n$ in the region below 650 cm.$^{-1}$ [15,16] were referred to for the adjustments of potential constants. The final set of the potential constants and their standard errors[28b] are listed in Table I. A common stretching of internal-rotation constants were used for the axial and equatorial bonds since the arrangements of the carbon and hydrogen atoms adjacent to these C—C bonds are the same as shown in Figure 6. The internal-rotation constants for the main chain C—C bonds and for the C-methyl bond correspond to the threefold potential barrier as high as 5.6 ± 1.4 and 2.9 ± 0.1 kcal./mole, respectively (approximately corrected for anharmonicity). In the least square treatments, the elements of Jacobian matrices (derivatives of frequencies with

respect to potential constants) were calculated by the equation reported previously.[29]

The frequencies of $[—CH_2—CH(CH_3)—]_n$ calculated with the set of the potential constants of Table I are listed in comparison with the observed frequencies in Tables II–IV.[28c] As shown in these tables, the calculated frequencies agreed closely with the observed frequencies, therefore, the

TABLE I
Modified Urey-Bradley Potential Constants (and Standard Error[a]) of Isotactic Polypropylene

Constant	Value	Assignment
K(C—H), stretching, mdyne/A.	4.255 ± 0.003	CH_3 group
	3.980 ± 0.005	CH_2 group
	4.030 ± 0.003	CH group
K(C—C), stretching, mdyne/A.	2.240 ± 0.108	CH—CH_2 bond
	2.270 ± 0.110	CH—CH_3 bond
Y(C—C), internal rotation, mdyne/A.	0.176 ± 0.042	CH—CH_2 bond
	0.080 ± 0.002	CH—CH_3 bond
H(H—C—H), bending, mdyne/A.	0.366 ± 0.002	CH_3 group
	0.353 ± 0.004	CH_2 group
H(H—C—C), bending, mdyne/A.	0.231 ± 0.011	CH_3 group
	0.218 ± 0.006	CH_2 group
	0.235 ± 0.016	CH group
H(C—C—C), bending, mdyne/A.	0.350 ± 0.100	C—CH_2—C angle
	0.390 ± 0.035	C—CH—C angle
F(H—C—H), repulsion, mdyne/A.	0.200[b]	
F(H—C—C), repulsion, mdyne/A.	0.480[b]	
F(C—C—C), repulsion, mdyne/A.	0.280 ± 0.065	
κ, intramolecular tension, mdyne/A.	−0.028 ± 0.008	CH_3 group
	0.002 ± 0.012	CH_2 group
	−0.130 ± 0.055	CH group
T, *trans*-coupling, mdyne/A.	0.118 ± 0.007	H—C—C—H
G, *gauche*-coupling, mdyne/A.	−0.038 ± 0.007	H—C—C—H
p(C—H), stretching interaction, mdyne/A.	−0.115 ± 0.005	CH_3 group
	−0.115 ± 0.015	CH_2 group
l(C—C—H), angle interaction, mdyne/A.	0.000 ± 0.005	C—CH_2—C

[a] Reference 28b.
[b] Transferred from ethane.[27]

normal modes and the potential energy distributions were also calculated. In Tables II and III, the potential energy distributions $(PED)_{ti}$ are listed for the vibrations of polypropylene below 1500 cm.$^{-1}$, where only the terms greater than 15% are listed. The numerical computation works in our recent studies are carried out with NEAC 2206 and 2101 digital computers (Nippon Electric Co. Ltd.).

TABLE II
The Observed and Calculated Frequencies and Potential Energy Distributions of Isotactic Polypropylene in the Region 1500–600 cm.$^{-1}$

Frequency, cm.$^{-1}$		
ν_{Obs}[a,b]	ν Calc.	Potential energy distributions, %[c]
1460 (s, $\perp$)	1463 $\nu_7(E)$	CH_3 δ_a (eq: 70, ax: 10)
	1462 $\nu_7(A)$	CH_3 δ_a (eq: 50, ax: 30)
1454 (m, $\parallel$)	1461 $\nu_8(A)$	CH_3 δ_a (ax: 50, eq: 30)
	1461 $\nu_8(E)$	CH_3 δ_a (ax: 75, eq: 10)
1435 (m, $\perp$)	1439 $\nu_9(E)$	CH_2 bend. (100)
	1436 $\nu_9(A)$	CH_2 bend. (100)
1378 (m, $\parallel$)	1385 $\nu_{10}(A)$	CH_3 δ_s (90)
1377 (s, $\perp$)	1386 $\nu_{10}(E)$	CH_3 δ_s (85)
1365 (vw, $\parallel$)	1367 $\nu_{11}(A)$	CH_2 wag. (40), CH_3 δ_s (15), CH bend.^{ax} (30)
1360 (m, $\perp$)	1365 $\nu_{11}(E)$	CH_2 wag. (15), CH_3 δ_s (15), CH bend^{eq} (30), CH_2 twist (20)
1330 (w, $\perp$)	1344 $\nu_{12}(E)$	CH_2 wag. (35), CH bend.^{ax} (35)
1326 (vw, $\parallel$)	1332 $\nu_{12}(A)$	CH bend.^{eq} (60)
1304 (m, $\parallel$)	1304 $\nu_{13}(A)$	CH_2 wag. (50), CH_2 twist. (25), CH bend.^{ax} (15)
1296 (w, $\perp$)	1301 $\nu_{13}(E)$	CH bend. (ax: 20, eq: 20), CH_2 wag. (40)
1254 (m, $\parallel$)	1264 $\nu_{14}(A)$	CH_2 twist. (35), CH bend. (ax: 20, eq: 10)
1220 (w, $\perp$)	1195 $\nu_{14}(E)$	CH_2 twist. (25), CH bend. (15), r_{CC}^{eq} (20)
1168 (s, $\parallel$)	1165 $\nu_{15}(A)$	r_{CC}^{ax} (40), CH_3 rock^{ax} (25)
1155 (m, $\perp$)	1166 $\nu_{15}(E)$	r_{CM} (20), CH bend. (15)
1103 (m, $\perp$)	1112 $\nu_{16}(E)$	CH_3 rock (ax: 20, eq: 10), r_{CC}^{ax} (25)
1045 (m, $\parallel$)	1051 $\nu_{16}(A)$	r_{CM} (35), r_{CC}^{eq} (30)
1034 (vw, $\perp$)	1021 $\nu_{17}(E)$	r_{CM} (30), CH_3 rock^{eq} (15), CH_2 twist. (15), CH bend. (15)
998 (s, $\parallel$)	996 $\nu_{17}(A)$	CH_3 rock.^{eq} (35), r_{CM} (35), CH bend. (15), CH_2 twist. (15)
973 (s, $\parallel$)	950 $\nu_{18}(A)$	CH_3 rock.^{ax} (50), r_{CC}^{ax} (20), r_{CC}^{eq} (20)
941 (w, $\perp$)	930 $\nu_{18}(E)$	CH_3 rock. (ax: 35, eq: 10), r_{CC}^{ax} (35)
899 (m, $\perp$)	892 $\nu_{19}(E)$	CH_3 rock.^{eq} (35), CH_2 rock. (20), CH bend^{eq} (15)
842 (s, $\parallel$)	862 $\nu_{19}(A)$	CH_3 rock (ax: 10, eq: 25); r_{CC}^{eq} (30)
	833 $\nu_{20}(A)$	CH_2 rock. (75), CH bend.^{ax} (15)
809 (m, $\perp$)	818 $\nu_{20}(E)$	CH_2 rock. (35), r_{CM} (25), r_{CC}^{eq} (20)

[a] Data from Peraldo and Farina.[1]

[b] Terms in parentheses denote intensity (s, strong; m, medium; w, weak; and vw very weak) and dichroism ($\parallel$, parallel band; and $\perp$, perpendicular band).

[c] CH_3 δ_s and CH_3 δ_a denote the symmetric and asymmetric deformation modes (Fig. 5), respectively, of the methyl group; r_{CM}, C-methyl stretching; r_{CC}^{ax} and r_{CC}^{eq}, axial and equatorial C—C stretching modes, respectively.

CH_2 BENDING VIBRATIONS

The band of polypropylene at 1435 cm.$^{-1}$ is also observed for [—CH_2—$CD(CH_3)$—]$_n$ and [—CH_2—$CH(CD_3)$—]$_n$ but not for [—CD_2—$CH(CH_3)$—]$_n$, and has been assigned to the CH_2 bending vibration.[1,5] As

TABLE III
The Frequencies of the Far Infrared Bands and the Potential Energy Distributions of Isotactic Polypropylene

Frequency, cm.$^{-1}$			Potential energy distribution, %[b]
ν_{Obs}[a]	ν_{Calc}		
528 ($\perp$)	$\nu_{21}(E)$	509	δ^a (40), δ (25)
460 ($\perp$)	$\nu_{22}(E)$	445	δ^a (65)
456 ($\parallel$)	$\nu_{21}(A)$	473	δ^a (75)
398 ($\parallel$)	$\nu_{22}(A)$	392	δ^a (35), δ^a (40)
321 ($\perp$)	$\nu_{23}(E)$	314	δ^a (60)
251 ($\parallel$)	$\nu_{23}(A)$	272	δ^a (40), δ^a (20)
210 ($\perp$)	$\nu_{24}(E)$	207	t_{C-CH_3} (95)
200 ($\parallel$)	$\nu_{24}(A)$	203	t_{C-CH_3} (85)
169 ($\perp$)	$\nu_{25}(E)$	162	δ^a (40), δ (30), t_{CC}^{ax} (15)
155 ($\parallel$)	$\nu_{25}(A)$	157	δ (40), t_{CC}^{eq} (35)
106	$\nu_{26}(E)$	90	t_{CC}^{ax} (70)

[a] Data (observed) of Miyazawa.[12,16]

[b] δ^s and δ^a denote the symmetric and asymmetric deformation modes of the C—CH-(C)—C group; δ, C—CH_2—C bending; t_{CC}^{ax}, t_{CC}^{eq}, and t_{C-CH_3}, the internal rotation modes about the axial and equatorial C—C bonds and the C-methyl bond, respectively.

TABLE IV
Frequencies (Intensity and Dichroism) of the Observed Bands and the Calculated Frequencies and Vibrational Assignments for Isotactic Polypropylene

Frequency, cm.$^{-1}$		Vibrational assignments
ν_{Obs}[a,b]	ν_{Calc}	
2959 (vs, $\parallel$)	2962 $\nu_1(A)$ 2962 $\nu_1(E)$	CH_3 asym. stretching (antisym. with respect to the H—C—CH_3 plane)
2950 (vs, $\perp$)	2962 $\nu_2(E)$ 2962 $\nu_2(A)$	CH_3 asym. stretching (sym. with respect to the H—C—CH_3 plane)
2921 (vs, $\perp$)	2927 $\nu_3(E)$ 2926 $\nu_3(A)$	CH stretching
2879 (s, $\perp$)	2903 $\nu_4(E)$ 2906 $\nu_4(A)$	CH_2 antisym. stretching
2868 (s, $\perp$)	2873 $\nu_5(E)$ 2873 $\nu_5(A)$	CH_3 sym. stretching
2838 (m)	2848 $\nu_6(E)$ 2845 $\nu_6(A)$	CH_2 sym. stretching

[a] Data from Peraldo and Farina.[1]

[b] Terms in parentheses denote intensity (vs, very strong; s, strong; m, medium) and dichroism ($\parallel$, parallel band; $\perp$, perpendicular band).

shown in Table II the potential energy of this vibration is almost exclusively associated with the CH_2 bending mode.

For [—CH_2—CH(CD_3)—]$_n$, the bands due to the A and E components have been resolved at 1440 ($\parallel$) and 1438 cm.$^{-1}$ ($\perp$), respectively.[1] The infrared intensity ratio for these CH_2 bending vibrations has been cal-

culated to be $A:E = 1.8:1$.[2] In fact, the parallel peak at 1440 cm.$^{-1}$ has been found to be slightly stronger than the perpendicular peak at 1438 cm.$^{-1}$ (Fig. 4f of ref. 1).

For either of [—CH_2—$CH(CH_3)$—]$_n$ and [—CH_2—$CD(CH_3)$—]$_n$, the band at 1435 cm.$^{-1}$ has not been resolved into two components.[1] The strong perpendicular dichroism of the band at 1435 cm.$^{-1}$ indicates that the A component is appreciably weaker than the E component; the observed intensity ratio ($A:E$) is much different from the ratio estimated from the spatial structure or from the ratio observed for [—CH_2—$CH(CD_3)$—]$_n$. Since the spatial structure of isotactic polypropylene will not change much upon isotopic substitutions, the intensity reduction of the A component is possibly associated with changes in the normal mode. From the analysis of the normal mode, the hybridization of the methyl asymmetric deformation mode is found to be greater for the CH_2 bending vibration (ν_9) of the A species than for the corresponding ν_9 vibration of the E species. In fact, slight coupling of the CH_3 asymmetric deformation modes is also suggested from the higher frequency shift of the CH_2 bending band upon the deuteration of the methyl group.

CH_3 DEFORMATION VIBRATIONS

Asymmetric Deformation Modes

The parallel band at 1454 cm.$^{-1}$ and the perpendicular band at 1460 cm.$^{-1}$ of polypropylene are also observed for [—CH_2—$CD(CH_3)$—]$_n$ and [—CD_2—$CH(CH_3)$—]$_n$, but not for [—CH_2—$CH(CD_3)$—]$_n$. Therefore these bands have been assigned to the asymmetric deformation vibrations of the methyl groups.[1,5] Either of the bands at 1460 and 1454 cm.$^{-1}$ has not been resolved into two components and the dichroism is not strong. Apparently, the 1460 cm.$^{-1}$ ($\perp$) band due to the E vibration is overlapped by the corresponding band due to the A vibration, and the 1454 cm.$^{-1}$ ($\parallel$) band due to the A vibration is overlapped by the corresponding band due to the E vibration.

Symmetric Deformation Modes

For [—CH_2—$CH(CH_3)$—]$_n$, the strong perpendicular band at 1377 cm.$^{-1}$ and the medium intensity band at 1378 cm.$^{-1}$ are primarily due to the methyl symmetric deformation mode (Table II). The intensity ratio of the parallel and perpendicular bands has been estimated by Krimm[2] to be 0.4:1.0, in good agreement with the observed intensity ratio.[1]

NORMAL VIBRATIONS OF POLYPROPYLENE [—CH_2—$CH(CH_3)$—]$_n$

CH_2 Wagging and Twisting Modes and CH Bending Modes

As listed in Table II, four parallel bands and four perpendicular bands have been observed for [—CH_2—$CH(CH_3)$—]$_n$[1] in the region between 1370

and 1200 cm.$^{-1}$. Similar spectra have also been observed for [—CH_2—CH(CD_3)—]$_n$, but not for either [—CH_2—$CD(CH_3)$—]$_n$ or for [—CD_2—$CH(CH_3)$—]$_n$. In view of the potential energy distributions (Table II), these bands of polypropylene are found to arise from the hybridized vibrations of the CH_2 wagging and twisting modes and the axial and equatorial CH bending modes.

On deuteration of the CH group, two parallel bands (at 1342 and 1291 cm.$^{-1}$) have been observed for [—CH_2—$CD(CH_3)$—]$_n$.[1] These bands are due to the CH_2 wagging and twisting modes which are not coupled with the CH bending modes.[20] On the other hand, for [—CD_2—$CH(CH_3)$—]$_n$, two parallel bands (1327 and 1313 cm.$^{-1}$) and two perpendicular bands (1325 and 1303 cm.$^{-1}$) have been observed.[1] These bands arise from the CH bending modes which are free from coupling with either the CH_2 wagging or twisting modes. These "intrinsic" CH_2 wagging and twisting vibrations and CH bending vibrations all lie in the narrow region of 1340–1270 cm.$^{-1}$ and accordingly couple extensively with one another for the molecule of [—CH_2—$CH(CH_3)$—]$_n$.

The weak parallel band at 1254 cm.$^{-1}$ and the weak perpendicular band of polypropylene at 1220 cm.$^{-1}$ were previously considered to arise from the CH_2 twisting modes. Actually, however, these frequencies are much lower than the intrinsic CH_2 twisting frequencies as observed for [—CH_2—$CD(CH_3)$—]$_n$. The potential energy distributions indicate that these bands of polypropylene are due to the twisting modes being coupled with the CH bending modes.

CH_3 and CH_2 Rocking Modes and C—C Stretching Modes

In the region between 1200 and 900 cm.$^{-1}$, five strong parallel bands due to the A vibrations and five perpendicular bands due to the E vibrations are observed.[1] As shown in Table II, these bands of polypropylene arise from the hybridized vibrations of the axial and equatorial methyl rocking modes, the axial and equatorial C—C stretching modes, the C-methyl stretching mode, and the CH_2 rocking mode.

The strong parallel bands at 1168, 998, and 973 cm.$^{-1}$ are more or less associated with the methyl rocking modes as shown in Table II. However, the hybridizations of the C—C stretching modes are appreciable for these vibrations. Thus the band at 1168 cm.$^{-1}$ is primarily associated with the axial C—C stretching mode as coupled with the methyl rocking mode. The band at 1045 cm.$^{-1}$ is due to the asymmetric stretching mode of the C-methyl bond and the equatorial C—C bond. The band at 998 cm.$^{-1}$ is due to the methyl rocking mode as coupled with the C-methyl stretching mode whereas the band at 973 cm.$^{-1}$ is due to the methyl rocking mode as coupled with the antisymmetric stretching mode of the axial and equatorial C—C bonds. The parallel band at 842 cm.$^{-1}$ corresponds either to the $\nu_{19}A$ vibration or to the $\nu_{20}A$ vibration.

The perpendicular band of polypropylene at 1155 cm.$^{-1}$ has also been observed in the Raman effect.[30] This band is assigned to the $\nu_{15}(E)$ vibra-

tion calculated at 1166 cm.$^{-1}$. Although the $\nu_{15}(E)$ and $\nu_{15}(A)$ vibrations lie closely with each other, the nature (potential energy distributions) of these vibrations are quite different. Thus the $\nu_{15}(E)$ vibration is primarily associated with the C-methyl stretching mode and the CH bending mode, but not much associated with the methyl rocking mode or with the axial C—C stretching mode. On the other hand, the perpendicular bands at 941 and 899 cm.$^{-1}$ are largely associated with the methyl rocking modes. The perpendicular band at 809 cm.$^{-1}$ is due to the CH_2 rocking mode (ϵ = 0°), coupled with the C-methyl stretching mode (ϵ = −40°) and the equatorial C—C stretching mode (ϵ = 25°).

NORMAL VIBRATIONS OF POLYPROPYLENE-2-*d* [—CH_2—$CD(CH_3)$—]$_n$

CH_2 Wagging and Twisting Modes

From the analyses of the potential energy distributions, the parallel band of [—CH_2—$CD(CH_3)$—]$_n$ at 1342 cm.$^{-1}$ and the perpendicular band at 1334 cm.$^{-1}$ are found to be due almost exclusively to the CH_2 wagging modes. On the other hand, the parallel band at 1291 cm.$^{-1}$ and the perpendicular band at 1273 cm.$^{-1}$ are associated with the CH_2 twisting modes. The CH_2 wagging and twisting frequencies of propane are 1336 and 1278 cm.$^{-1}$, respectively.[24] These vibrations of propane are also free from much coupling with other modes. Therefore the intrinsic CH_2 wagging and twisting frequencies may be taken as about 1335 and 1280 cm.$^{-1}$, respectively.

CD Bending, CH_3 and CH_2 Rocking, and C—C Stretching Modes

For [—CH_2—$CD(CH_3)$—]$_n$, eight parallel bands [1210(m), 1145(m), 1060(w), 981(s), 969(s), 881(w), 790(s), and 754 cm.$^{-1}$ (m)] and six perpendicular bands [1179(w), 1091(w), 1005(w), 949(w), 821(m), and 781 cm.$^{-1}$(w)] have been observed[1] in the region 1250–650 cm.$^{-1}$. All these bands arise from the hybridized vibrations of the CD bending, CH_3 rocking, CH_2 rocking, and C—C stretching modes.[20] No single band is due to a "pure" mode. All these modes have their intrinsic frequencies in the region of 1100–800 cm.$^{-1}$. For highly symmetric molecules, symmetry elements (such as twofold axes or planes of symmetry) impose restrictions upon the vibrational couplings among those vibrational modes even though their intrinsic frequencies happen to lie in the same frequency region. However, the molecular chain of isotactic polypropylene and deuterated derivatives do not have such symmetry elements, and all those vibrational modes of [—CH_2—$CD(CH_3)$—]$_n$ are subject to extensive hybridization.

The parallel band at 1210 cm.$^{-1}$ is due to the antisymmetric stretching mode of the axial and equatorial C—C bonds as coupled with the CD bending mode.

The parallel bands at 1145 and 790 cm.$^{-1}$ are both due to the coupling of the CD bending mode and the methyl rocking mode (in the D—C-methyl plane). The perpendicular band at 821 cm.$^{-1}$ arises from the CD bending mode as coupled with the C-methyl stretching mode.

Two strong parallel bands at 981 and 969 cm.$^{-1}$ correspond to the $\nu_{16}(A)$ and $\nu_{17}(A)$ vibrations calculated at 974 and 955 cm.$^{-1}$. The $\nu_{16}(A)$ vibration is largely associated with the C-methyl stretching mode as coupled with the methyl rocking mode and CD bending mode whereas the $\nu_{17}(A)$ vibration is primarily due to the methyl rocking mode as coupled with the axial C—C stretching mode.

The CH_2 rocking mode of $[—CH_2—CD(CH_3)—]_n$ is strongly coupled with the CD bending modes and gives rise to the parallel band at 754 cm.$^{-1}$ and the perpendicular band at 781 cm.$^{-1}$.

NORMAL VIBRATIONS OF POLYPROPYLENE-1,1-d_2 $[—CD_2—CH(CH_3)—]_n$

CH Bending Modes

From the analyses of the potential energy distributions,[20] the parallel bands of $[—CD_2—CH(CH_3)—]_n$ at 1327 and 1313 cm.$^{-1}$ and the perpendicular bands at 1325 and 1303 cm.$^{-1}$ are almost exclusively due to the CH bending modes. The CH bending vibration of isobutane is observed at 1330 cm.$^{-1}$, which is not much coupled with other vibrational modes. Taking into account the CH bending frequencies of isobutane as well as of $[—CD_2—CH(CH_3)—]_n$, the "intrinsic" CH bending frequency may be taken as ca. 1320 cm.$^{-1}$.

CD_2 Rocking Modes

The parallel band at 691 cm.$^{-1}$ is primarily due to the CD_2 rocking mode. The perpendicular band at 716 cm.$^{-1}$ is due to the CD_2 rocking mode as coupled with the C-methyl stretching mode and the equatorial C—C stretching mode.

CD_2 Bending, Wagging, and Twisting Modes, CH_3 Rocking Modes, and C—C Stretching Modes

For $[—CD_2—CH(CH_3)—]_n$, seven parallel bands [1184(s), 1134(m), 1058(s), 1013(s), 894(m), 868(s), and 764 cm.$^{-1}$(w)] and seven perpendicular bands [1170(m), 1110(m), 1051(m), 1018(m), 896(w), 868(w), and 811 cm.$^{-1}$(w)] have been observed[1] in the region 1200–750 cm.$^{-1}$. These bands arise from the hybridized vibrations of the CD_2 bending, wagging, and twisting modes, methyl rocking modes, and C—C stretching modes.[20]

The parallel band at 1058 cm.$^{-1}$ and the perpendicular band at 1051 cm.$^{-1}$ appear to correspond to the $\nu_{15}(A)$ and $\nu_{15}(E)$ vibrations which are

calculated at 1052 and 1045 cm.$^{-1}$, respectively. These vibrations are associated primarily with the CD_2 bending mode.

The parallel band at 1184 cm.$^{-1}$ is due to the axial C—C stretching mode coupled with the CD_2 wagging mode whereas the perpendicular band at 1170 cm.$^{-1}$ is due to the equatorial C—C bond coupled with the CD_2 bending mode.

The parallel bands at 894 and 868 cm.$^{-1}$ are due to the methyl rocking modes as coupled with the CD_2 wagging or twisting modes. The parallel band at 1013 cm.$^{-1}$ arises from the antisymmetric stretching mode of the C-methyl and equatorial C—C bonds as coupled with the CD_2 wagging and methyl rocking mode. For the degenerate species, the CD_2 wagging mode is coupled with the methyl rocking mode and gives rise to the perpendicular bands at 1110 and 1018 cm.$^{-1}$.

The weak parallel band at 764 cm.$^{-1}$ and the perpendicular band at 811 cm.$^{-1}$ are primarily due to the CD_2 twisting mode.

NORMAL VIBRATIONS OF POLYPROPYLENE-3,3,3-d_3 [—CH_2—$CH(CD_3)$—]$_n$

CH_2 Wagging and Twisting Modes and CH Bending Modes

For isotactic [—CH_2—$CH(CD_3)$—]$_n$, four parallel bands [1379(w), 1334(w), 1305(m), and 1239 cm.$^{-1}$(m)] and four perpendicular bands [1361(m), 1333(m), 1293(m), and 1206 cm.$^{-1}$(w)] have been observed[1] in the region 1400–1200 cm.$^{-1}$. These bands arise from the couplings of the CH_2 wagging, CH bending, and CH_2 twisting modes, much similar to the case of [—CH_2—$CH(CH_3)$—]$_n$.

CD_3 Asymmetric Deformation Modes

The strong parallel band of [—CH_2—$CH(CD_3)$—]$_n$ at 1051 cm.$^{-1}$ corresponds to the $\nu_{14}(A)$ and $\nu_{15}(A)$ vibrations (calculated at 1049 and 1045 cm.$^{-1}$, respectively) and the strong perpendicular band at 1054 cm.$^{-1}$ corresponds to the $\nu_{15}(E)$ and $\nu_{16}(E)$ vibrations (calculated at 1044 and 1040 cm.$^{-1}$, respectively). The potential energy of these vibrations are almost exclusively associated with the asymmetric deformation modes of the CD_3 group.

CD_3 Symmetric Deformation Mode

The CD_3 symmetric stretching mode of [—CH_2—$CH(CD_3)$—]$_n$ is strongly coupled with the C—C stretching modes. The weak parallel band at 1115 cm.$^{-1}$ appears to correspond to the $\nu_{13}(A)$ vibration (calculated at 1097 cm.$^{-1}$), which arises from the CD_3 symmetric deformation mode as coupled with the C-methyl stretching mode. The perpendicular band at 1081 cm.$^{-1}$ corresponds either to the $\nu_{13}(E)$ vibration calculated at 1085 cm.$^{-1}$ or to the $\nu_{14}(E)$ vibration calculated at 1064 cm.$^{-1}$. The $\nu_{14}(E)$ vibration is primarily due to the CD_3 symmetric deformation mode as coupled

with the asymmetric deformation mode. The parallel band at 989 cm.$^{-1}$ is due to the equatorial C—C stretching mode as coupled with the CD_3 symmetric deformation mode.

CD_3 Rocking Modes

The parallel bands at 791 and 703 cm.$^{-1}$ and the perpendicular bands at 759 and 743 cm.$^{-1}$ are associated almost exclusively with the CD_3 rocking modes as revealed by the calculation of the potential energy distributions. For the *A* vibration at 791 cm.$^{-1}$ and the *E* vibration at 759 cm.$^{-1}$, the CD_3 rocking mode is nearly perpendicular to the H—C-methyl plane, whereas for the *A* vibration at 703 cm.$^{-1}$ and the *E* vibration at 743 cm.$^{-1}$ the CD_3 rocking mode is nearly symmetric with respect to the H—C-methyl plane.

C—C Stretching Modes and CH_2 Rocking Mode

The parallel band at 909 cm.$^{-1}$ is due to the symmetric stretching mode of the C-methyl and equatorial C—C bonds. On the other hand, the strong perpendicular band at 1145 cm.$^{-1}$ is due to the C-methyl stretching mode and the CH bending mode. The perpendicular band at 821 cm.$^{-1}$ is due to the CH_2 rocking mode as coupled with the C-methyl and equatorial C—C stretching modes.

LIQUID SPECTRA OF ISOTACTIC POLYPROPYLENE AND DEUTERATED DERIVATIVES

On the basis of the potential energy distributions as well as the normal modes calculated for the crystalline spectra, one may also assign the bands observed in the liquid spectra of isotactic polypropylene and deuterated derivatives.[20]

Localized Modes

The effect of melting upon the infrared spectra of isotactic polypropylene[21,32] and deuterated derivatives[1] have been studied and several absorption bands have been found to persist upon melting. For example, strong bands are observed at 1380 and 1460 cm.$^{-1}$, for [—CH_2—CH(CH_3)—]$_n$, [—CH_2—CD(CH_3)—]$_n$, and [—CD_2—CH(CH_3)—]$_n$, but not for [—CH_2—CH(CD_3)—]$_n$,[1] and these peaks have been assigned to the symmetric and asymmetric deformation modes, respectively, of the methyl group. Similarly for [—CH_2—CH(CD_3)—]$_n$ in the liquid state, a strong band is observed at 1052 cm.$^{-1}$. This band corresponds to the strong bands at 1054 (parallel) and 1051 cm.$^{-1}$ (perpendicular) in the crystalline state, and is assigned to the asymmetric deformation modes of the CD_3 group in the liquid state.

The strong band at 1446 cm.$^{-1}$ is observed for [—CH_2—CH(CD_3)—]$_n$ and has been assigned to the CH_2 bending mode. For [—CH_2—CH-

$(CH_3)—]_n$ and $[—CH_2—CD(CH_3)—]_n$ in the liquid state, the band due to the CH_2 bending mode is overlapped by the strong band arising from the asymmetric methyl deformation modes. For $[—CD_2—CH(CH_3)—]_n$, a medium intensity band is observed at 1057 cm.$^{-1}$. This band appears to correspond to the $\nu_{15}(A)$ (1058 cm.$^{-1}$) and $\nu_{15}(E)$ (1051 cm.$^{-1}$) vibrations of the crystalline state and is assigned to the CD_2 bending mode.

The frequencies of the symmetric and asymmetric deformation vibrations of the methyl group or the bending vibrations of the methylene group essentially do not shift upon melting. The potential energy of these vibrations are concentrated in one vibrational mode and the atomic displacements are localized either in the methyl group or in the methylene group. Therefore, even though the main chain of isotactic polypropylene carries out internal-rotation rearrangements above the melting point, these localized vibrations of the methyl or the methylene groups are not much influenced by the thermal motions of the backbone chain. The bands arising from localized vibrations in the liquid state may be as strong and sharp (well-defined) as the corresponding bands in the crystalline state.

CH_2 Wagging and Twisting Modes

From these considerations, the bands due to localized vibrations in the liquid state will be stronger and more well-defined as the localization is higher. For $[—CH_2—CD(CH_3)—]_n$, a strong band has been observed at 1333 cm.$^{-1}$, and this is assigned to the CH_2 wagging mode in the liquid state. The CH_2 wagging mode of this molecule is free from much coupling with other modes and its vibrational displacements are much localized in the $C—CH_2—C$ group. The frequency of this band agrees closely with the intrinsic CH_2 wagging frequency taken as 1335 cm.$^{-1}$.

The liquid band of $[—CH_2—CD(CH_3)—]_n$ at 1282 cm.$^{-1}$ corresponds to the intrinsic CH_2 twisting frequency taken at 1280 cm.$^{-1}$ and is assigned to the CH_2 twisting mode in the liquid state. The twisting mode of this molecule is also free from much coupling with other vibrational modes.

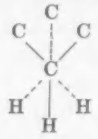
C—H Bending Modes

For $[—CD_2—CH(CH_3)—]_n$, a strong band is observed at 1318 cm.$^{-1}$ in the liquid state. This band corresponds to the intrinsic CH bending frequency of 1320 cm.$^{-1}$. The CH bending vibrations of this molecule are not much coupled with other vibrational modes.

For $[—CH_2—CH(CD_3)—]_n$ in the liquid state, four bands have been observed[1] at 1358, 1326 (shoulder), 1293, and 1235 cm.$^{-1}$. These peaks arise from the CH_2 wagging and twisting modes and CH bending modes in the liquid state. The observed frequencies, however, are shifted slightly but distinctly from the intrinsic frequencies of the vibrational modes concerned with.

The vibrational couplings between the CH and CH_2 modes should depend upon the internal-rotation conformations about the $CH—CH_2$ bonds.

If the three staggered conformations should be equally assumed for the main chain of isotactic polypropylene, the vibrational coupling effects would be smoothed out, and the intrinsic frequencies of the CH and CH_2 groups would appear. The observed shifts from the intrinsic frequencies possibly indicates that the high-energy conformation



is in fact less abundant than the other two more stable conformations for the isotactic polypropylene chains in the liquid state.

CD_3 Rocking Modes

For $[—CH_2—CH(CD_3)—]_n$ in the liquid state, two medium intensity bands are observed at 790 and 709 cm.$^{-1}$. The band at 790 cm.$^{-1}$ corresponds to the $\nu_{19}(A)$ (791 cm.$^{-1}$) and the $\nu_{19}(E)$ (759 cm.$^{-1}$) of the crystalline state and is assigned to the CD_3 rocking mode perpendicular to the H—C-methyl plane. On the other hand, the liquid band at 709 cm.$^{-1}$ corresponds to the $\nu_{20}(A)$ (703 cm.$^{-1}$) and $\nu_{20}(E)$ (743 cm.$^{-1}$) and is assigned to the CD_3 rocking mode in the H—C-methyl plane. The atomic displacements of these vibrations are possibly much localized, at least in the CD_3—CH(C)—C group. The internal rotation conformation of this group does not change by the rearrangements of the CD_3 group from one staggered form to another. Therefore the CD_3 rocking modes are not influenced by the internal rotation of the CD_3 group and well-defined bands due to the CD_3 rocking modes may well be expected even in the liquid state.

The CD_3 rocking frequencies of perdeuterated ethane, C_2D_6, are observed at 970 cm.$^{-1}$ (E_g) and 594 cm.$^{-1}$ (E_u). Since the splitting of these rocking frequencies arises from the *trans*- and *gauche*-coupling potential terms[22,24] the intrinsic CD_3 rocking frequency may be taken as the average value of about 780 cm.$^{-1}$. The CD_3 rocking frequency of $[—CH_2—CH(CD_3)—]_n$ at 790 cm.$^{-1}$ corresponds to the intrinsic frequency derived from deuteroethane. On the other hand, the lower frequency of the CD_3 rocking mode in the H—C-methyl plane is due to the *trans*- and *gauche*-interaction with the C—H bending mode.

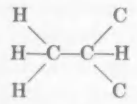
CH_3 Rocking and C—C Stretching Modes

For $[—CH_2—CH(CH_3)—]_n$ two strong bands are observed at 1151 and 971 cm.$^{-1}$ in the liquid state. These liquid bands are possibly associated with the vibrational modes of the CH_2—CH(C)—C group which are not influenced by the internal rotation rearrangements of the methyl group.

The intrinsic CH_3 rocking frequency may be estimated at about 1000 cm.$^{-1}$ from the methyl rocking frequencies of ethane (E_g = 1190 cm.$^{-1}$

and E_u = 821 cm.$^{-1}$). The liquid band of [—CH_2—CH(CH_3)—]$_n$ at 971 cm.^{1} lies close to this intrinsic frequency.

For tentative analyses of the liquid bands of [—CH_2—CH(CH_3)—]$_n$ the molecular vibrations of the group



have been calculated. The elements of the potential energy matrix have been transferred from the corresponding elements of isotactic polypropylene. In the region 1200–800 cm.$^{-1}$, three A' vibrations (symmetric with respect to the H—C-methyl plane) are calculated at 1062, 1015, and 864 cm.$^{-1}$ whereas two A'' vibrations (antisymmetric with respect to the H—C-methyl plane) are calculated at 1134 and 948 cm.$^{-1}$.

The liquid frequencies of isotactic polypropylene at 1151 and 971 cm.$^{-1}$ closely correspond to the calculated A'' frequencies, but not to any of the A' frequencies. The potential energy of the A'' vibration calculated at 1134 cm.$^{-1}$ is associated 50% with the C—CH—C antisymmetric stretching mode and 20% with the antisymmetric CH_3 rocking mode while the potential energy of the vibration calculated at 948 cm.$^{-1}$ is associated 40% with the C—CH—C stretching mode and 60% with the rocking mode. If one of these antisymmetric modes of vibration is excited in phase throughout the chain, the vibrations of adjacent units will tend to displace the common CH_2 group in nearly the same direction (at least not in the opposite direction). Only minor vibrational interactions may be expected between the two adjacent units. Such a vibrational mode may not be much sensitive to the change in the internal rotation rearrangements and accordingly may well give rise to well-defined strong absorption band even in the liquid state. More extensive analyses of the liquid spectra of isotactic polypropylene and deuterated derivatives will be important for conformation studies of isotactic polymeric chains, and accordingly theoretical developments for the treatments of liquid spectra of flexible polymeric chains are highly desirable.

NORMAL VIBRATIONS OF ISOTACTIC POLYPROPYLENE IN THE LOW FREQUENCY REGION

In the far infrared region of 600–800 cm.$^{-1}$, five parallel bands and five perpendicular bands of isotactic polypropylene have been observed[12,16] as shown in Table III. The dichroism of the band at 106 cm.$^{-1}$ has not been measured. However, all those bands may be reasonably assigned to the ν_{21}–$\nu_{25}(A)$ and ν_{21}–$\nu_{26}(E)$ vibrations.

The low frequency vibrations of isotactic polypropylene arise from the C—C—C bending modes of the C—CH_2—C group and the C—CH(C)—C group, and the internal rotation modes about the axial and equatorial C—C bonds and the C-methyl bond. The weak parallel band at 200 cm.$^{-1}$

and the perpendicular band at 210 cm.$^{-1}$ are due to the internal rotation mode of the methyl group. The internal rotation mode about the equatorial C—C bond is involved in the A vibration at 155 cm.$^{-1}$. The band at 106 cm.$^{-1}$ corresponds to the $\nu_{26}(E)$ vibration calculated at 90 cm.$^{-1}$. The frequency deviation may be ascribed partly to the neglect of the interchain potential energy. The low frequency bands of isotactic polypropylene arise from skeletal bending modes and/or the internal rotation modes. These modes are not localized in a single repeating unit, and accordingly give rise to well-defined bands only for highly ordered helical conformation of isotactic polypropylene.

cis-OPENING POLYMERIZATION OF POLYPROPYLENE AND NORMAL VIBRATIONS OF DIISOTACTIC POLYPROPYLENE-1-d_1

A number of poly(alkyl alkenyl ethers) were synthesized by Natta et al.[33] The x-ray diffraction of fibers of poly(*trans*-propenyl isobutyl ether) was studied and this polymer was found to be *threo*-diisotactic.[34] Thus the polymerization of propenyl alkyl ethers was found to occur by the *cis*-opening of the double bond. In this connection it is interesting to inquire whether the polymerization of propylene with Ziegler-Natta catalysts occurs also by the *cis*-opening of the double bonds or by the *trans*-opening.

Poly-*cis*-propylene-1-d_1 and poly-*trans*-propylene-1-d_1 were synthesized,[35] and the polarized infrared spectra (4000–600 cm.$^{-1}$) of these polymers were found to be quite different from each other, indicating that the structure

TABLE V

Observed Frequencies (Intensity and Dichroism) of Poly-*trans*-propylene-1-d_1 and the Calculated Frequencies and Potential Energy Distributions of *Threo* Diisotactic Polypropylene-1-d_1

Frequency, cm.$^{-1}$		
ν_{Obs}[a,b]	ν_{Calc}	Potential energy distribution, %
1340 (w, $\perp$)	$\nu_{10}(E)$ 1342	CH bend. (35), CH_3 δ_s (15) CHD wag. twist. (40)
1321 (ms, $\perp$)	$\nu_{11}(E)$ 1323	CHD bend. (35), CH bend. (50)
1290 (s, $\perp$)	$\nu_{12}(E)$ 1284	CHD bend. (65), CH bend. (20)
1253 (m, $\parallel$)	$\nu_{13}(A)$ 1256	CHD bend. (55), CH bend. (35)
1180 (s, $\parallel$)	$\nu_{14}(A)$ 1163	r_{CC}^{ax} (50), CH_3 rock. (15)
1076 (m, $\parallel$)	$\nu_{15}(A)$ 1082	CH_3 rock. (30), r_{CC}^{eq} (20),
1038 (m, $\parallel$)	$\nu_{16}(A)$ 1024	r_{CM} (65), CHD wag. (25)
993 (s, $\parallel$)	$\nu_{17}(A)$ 960	CH_3 rock. (45), CHD twist. (15), r_{CC}^{ax} (15), r_{CC}^{eq} (15)
950 (mw, $\perp$)	$\nu_{17}(E)$ 939	CH_3 rock. (40), CHD twist. (20)
749 (m, $\perp$)	$\nu_{20}(E)$ 755	CHD rock. (55), r_{CC}^{eq} (15)
719 (m, $\parallel$)	$\nu_{20}(A)$ 717	CHD rock. (75)

[a] Data of Peraldo and Farina.[1]

[b] Terms in parentheses denote intensity (s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak) and dichroism ($\parallel$, parallel band; $\perp$, perpendicular band).

TABLE VI

Observed Frequencies (Intensity and Dichroism) of Poly-*cis*-propylene-1-d_1 and the Calculated Frequencies and Potential Energy Distributions of *Erythro* Diisotactic Polypropylene-1-d_1

Frequency, cm.$^{-1}$		
ν_{Obs}[a,b]	ν_{Calc}	Potential energy distribution, %
1360 (s, $\perp$)	$\nu_{10}(E)$ 1358	CHD wag. twist. (45), CH bend. (35)
1313 (w, $\perp$)	$\nu_{11}(E)$ 1321	CH bend. (50), CHD bend. (20), CH_3 δ_s (15)
1286 (m, $\perp$)	$\nu_{12}(E)$ 1285	CHD bend. (75), CH bend. (15)
1273 (s, $\parallel$)	$\nu_{13}(A)$ 1266	CHD bend. (70), CH bend. (20)
1173 (s, $\parallel$)	$\nu_{14}(A)$ 1154	r_{CC}^{ax} (30), r_{CC}^{ex} (20), CH_3 rock. (15), CHD wag. twist. (20)
1121 (s, $\parallel$)	$\nu_{15}(A)$ 1114	CH_3 rock. (25), CHD wag. twist. (15), r_{CM} (15)
1033 (m, $\parallel$)	$\nu_{16}(A)$ 1037	r_{CM} (40), r_{CC}^{eq} (30)
990 (mw, $\perp$)	$\nu_{17}(E)$ 964	CH_3 rock. (30), CHD twist. (30), r_{CC}^{ax} (25)
975 (m, $\parallel$)	$\nu_{17}(A)$ 964	CH_3 rock. (55), r_{CC}^{ax} (15), r_{CC}^{eq} (15)
746 (s, $\parallel$)	$\nu_{20}(A)$ 738	CHD rock. (80)
736 (m, $\perp$)	$\nu_{20}(E)$ 740	CHD rock. (50), r_{CM} (20)

[a] Data of Peraldo and Farina.[1]

[b] Terms in parentheses denote intensity (s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak) and dichroism ($\parallel$, parallel band; $\perp$, perpendicular band).

(or the positions of the deuterium atoms) of these polymers are different too.[1]

In our previous study,[36] the infrared active A vibrations of the *threo* and *erythro* diisotactic polypropylene-1-d_1 were calculated with the potential constants as transferred from other hydrocarbons.[12] The calculated frequencies for the *threo* and *erythro* structures were found to correspond to the frequencies of the parallel bands observed for poly-*trans*-propylene-1-d_1 and poly-*cis*-propylene-1-d_1, respectively. Thus the polymerization of propylene with Ziegler-Natta catalysts has also been found to occur by the *cis*-opening of the double bond. This conclusion has been confirmed by a

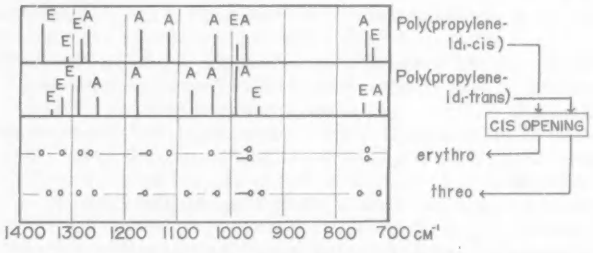


Fig. 7. Frequencies and relative intensities of the bands observed for poly-*cis*-propylene-l-d_1 and poly-*trans*-propylene-l-d_1 and the frequencies calculated for the *erythro* and *threo* diisotactic polypropylene-l-d_1.

more recent normal coordinate analysis. The A and $E(2\pi/3)$ vibrations of the *threo* and *erythro* structures have been calculated with the potential constants as adjusted by the method of least squares.[20] Calculated frequencies and potential energy distributions are listed in Tables V and VI, together with the observed frequencies (intensity and dichroism).[1] In those tables are collected only those observed bands which are strong enough for correlation tests. It may be seen that the frequencies calculated for the *threo* and *erythro* structure agree closely with the frequencies observed for poly-*trans*-l-d_1 and poly-*cis*-propylene-l-d_1, respectively. Especially, the correlations are conclusive for the $\nu_{15}(A)$, $\nu_{20}(A)$, $\nu_{10}(E)$, $\nu_{17}(E)$, and ν_{2c} (E) vibrations. The frequency comparisons are also provided in Figure 7.

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Discussion

J. R. Nielsen (*University of Oklahoma, Norman, Oklahoma, U.S.A.*): I have heard that in Japan you have obtained a Raman spectrum of polypropylene. How do the results support the analysis that you have presented here?

T. Miyazawa: We have not measured the Raman spectrum of isotactic polypropylene. In my calculations I have then used the data reported by Dr. Tobin a few years ago. His Raman frequencies appeared to correspond to perpendicular infrared bands of isotactic polypropylene. I wonder why the Raman lines due to the *A* fundamentals cannot be much stronger than the lines which have been actually observed.

S. Krimm (*University of Michigan, Ann Arbor, Michigan, U.S.A.*): I am sure I express the admiration of all of us for this very beautiful analysis of the normal vibrations of polypropylene. A window has been opened to the future study of polymer spectra. I wanted to ask one small question about the two bands that were briefly referred to as remaining in the spectrum of, shall we call it, liquid polypropylene at about 1171 and 950 cm.$^{-1}$. From your analysis of the crystalline polypropylene it turns out that there are two strong bands near 973 and 998 cm.$^{-1}$ which both seem to contain about the same contribution of methyl rocking and C—C equatorial stretching. They seem to be very similar bands in the crystalline polypropylene and yet when one goes to the liquid state, the band at 998 cm.$^{-1}$ almost completely disappears whereas the 975 cm.$^{-1}$ band still remains relatively intense in the spectrum. Is it possible to understand the rather different behavior of these two bands from a normal coordinate analysis.

My second question is the following: why are both the 973 and 1171 cm.$^{-1}$ bands completely absent in the atactic material?

T. Miyazawa: In answer to Dr. Krimm's first question, I would like to point out that the normal modes (or the atomic displacements) of the two vibrations at 973 and 998 cm.$^{-1}$ are quite different (see below) although in terms of the potential energy distributions these vibrations are much the same. The liquid bands at 1151 and 971 cm.$^{-1}$ appear to correspond to the crystalline bands at 1168 and 973 cm.$^{-1}$. As shown in the text, these vibrations may well give rise to well-defined bands even in the liquid state.

S. Califano (*Universita di Napoli, Naples, Italy*): I would like to add one comment to Dr. Miyazawa's paper. It is well known that the Urey-Bradley force field generally exaggerates the coupling between stretching and bending modes. Could this be a possible explanation to Dr. Krimm's question?

T. Miyazawa: The two bands at 973 and 998 cm.$^{-1}$ are quite different as for the normal mode. The vibration at 998 cm.$^{-1}$ is associated with the methyl rocking mode (in the H—C-methyl plane) as coupled with the C-methyl stretching mode whereas the vibration at 973 cm.$^{-1}$ is associated with the methyl rocking mode (out of the H—C-methyl plane) and the asymmetric stretching of the equatorial and axial C—C bonds.

J. H. Schachtschneider (*Shell Development Co., Emeryville, Calif., U.S.A.*): The potential energy distributions that Dr. Miyazawa has obtained for these two modes are very similar to ours. However, the 998 cm.$^{-1}$ mode, in addition to the methyl rocking and the C—C methyl stretching, has some coupling with the C—H bond; a small

amount but it is significant and this is possibly an explanation. As for Dr. Califano's comment about the Urey-Bradley field exaggerating the coupling between bending and stretching, we find that the valence force field gives a very similar type of coupling. There is in general a very strong coupling between methyl rocking and stretching.

P. Pino (*Universita di Pisa, Pisa, Italy*): I would like to emphasize the importance of the results obtained by Dr. Miyazawa from the calculations of the spectra of the *erythro* diisotactic deutero polypropylene. This is probably the first real experimental evidence about the nature of the *cis* addition in the polymerization process of the olefins. Such a kind of addition has been demonstrated for the case of the alkenyl ethers, but in this case one could always think that the oxygen atom (always present in that class of compounds) could form some sort of complex with the catalyst and could somehow influence the stereospecificity of the process. From Dr. Miyazawa's results, it appears that also in the α-olefins a *cis* opening of the double bond is involved.

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Normal Vibrations of Polyethylene and Some Vinyl Polymers

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One of the programs we are now carrying out in our laboratory is to obtain a consistent set of force constants which can explain all the vibrational frequencies of the following molecules: (*1*) CX_4, C_2X_6, and C_2H_4; (*2*) CH_3X, CH_3CH_2X, $(CH_3)_2CHX$, $(CH_3)_3CX$, and $CH_3(CH_2)_2X$; (*3*) XCH_2X, $X(CH_2)_2X$, and $X(CH_2)_3X$; and (*4*) *meso*- and *d,l*-CH_3—CHX—CH_2—CHX—CH_3 and $(-CH_2-CHX-)_n$, where X denotes H, F, Cl, Br, and I. Molecules with the CN, OH, —O—, —CO—, —CO—O—, or —CO—NH— group are also being studied. Deuterated molecules are also included, when their frequencies are available.

The results so far obtained have been summarized previously.[1] Although the present set of force constants is far from the ideal one, it can explain frequencies of many small molecules pretty satisfactorily.

In the course of this study it was often realized that the calculations of normal frequencies are very useful in solving various physicochemical problems. In the present paper some examples in the field of high polymer chemistry will be reviewed.

Polyethylene

Infrared and Raman spectra of polyethylene and saturated normal hydrocarbons in the solid state, where the molecules take the extended zigzag conformation, have now been completely interpreted. Almost conclusive assignments have been made, and a reasonable set of force constants has been obtained.[2–4]

Figure 1 summarizes the results. The frequencies of normal vibrations of the extended polymethylene chain can be expressed as functions of phase difference between two adjacent CH_2 groups. These functions are shown in the middle part of Figure 1. The phase difference admitted, δ_k, is determined by the number of methylene units, N, and is given by

$$\delta_k = \pi k/N + 1 \qquad k = 1, 2, \ldots, N$$

As shown in Figure 1, infrared spectra of solid *n*-$C_{23}H_{48}$ and *n*-$C_{23}H_{47}OH$, for example, can be explained by this frequency–phase difference relationship. The accordion vibrations ($k = 1$) appearing in the Raman spectra of solid hydrocarbons (6) can also be explained as ν_5 skeletal vibrations.

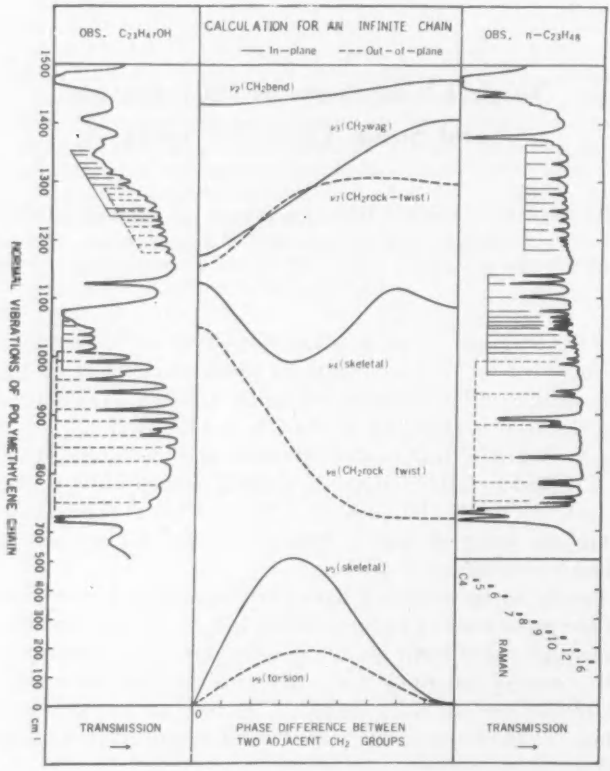


Fig. 1. Normal vibrations of the extended polymethylene chain. Spectra of n-$C_{23}H_{48}$ and $C_{23}H_{47}OH$ are taken from Snyder[5] and Tasumi et al.,[4] respectively.

Recently the Raman spectra of deuterated polyethylene have been measured by Brown.[8] The results are explained very well by our force constants, as shown in Figure 2.

The agreement between the observed and calculated frequencies for normal and deuterated polyethylenes suggests that the frequencies calculated for the partially deuterated polyethylenes with various configurations are also reliable. This means that we can determine the configuration of partially deuterated polyethylene by comparing the observed infrared spectra with the calculated frequencies. This method has been applied to the study of double bond opening in the ethylene polymerization reaction.[9,10]

Both *cis*- and *trans*-ethylene-d_2 will give polyethylenes with various configurations, as shown in Figure 3. If *cis*-ethylene-d_2 polymerizes by the *cis*-opening process, the spectra will be explained as a mixture of *erythro* diisotactic and disyndiotactic structures $(CHD—CHD)_n$. If it polymerizes

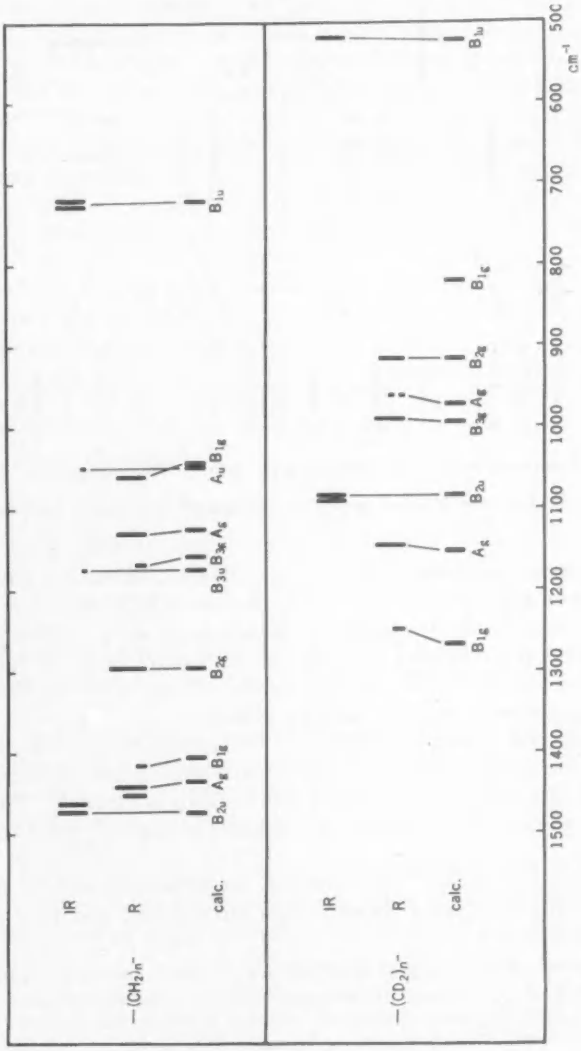


Fig. 2. Observed infrared and Raman[7,8] spectra and calculated frequencies of polyethylenes.

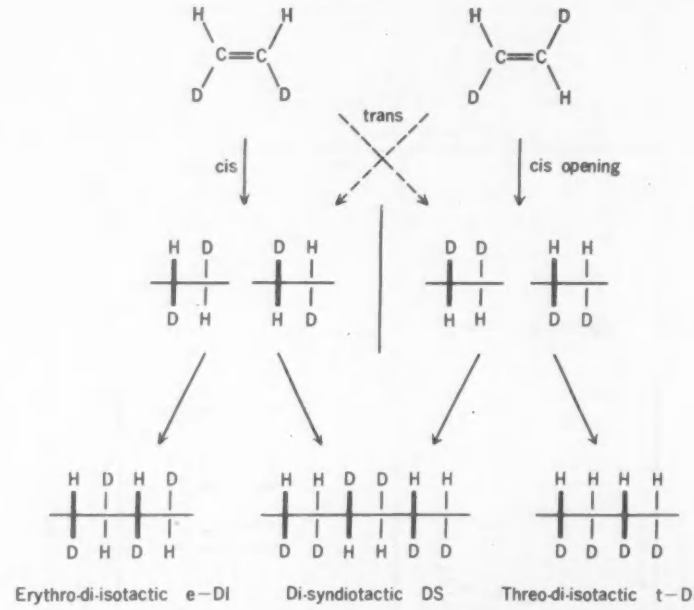


Fig. 3. Type of double bond opening and configuration of resultant polymer.

by the *trans*-opening process, the spectra will be explained as a mixture of disyndiotactic and *threo* diisotactic polyethylene $(CHD—CHD)_n$. In the case of *trans*-ethylene-d_2 the result will be reverse, as shown in Fig. 3. We have prepared polyethylenes from *cis*- and *trans*-ethylene-d_2 and compared their infrared spectra with the frequencies calculated for *erythro* diisotactic, disyndiotactic, and *threo* diisotactic isomers.

The result shows that *cis*-ethylene-d_2 produces the former two isomers and *trans*-ethylene-d_2 produces the latter two isomers if $Al(C_2H_5)_3$ and $TiCl_4$ are used as catalysts. A part of the result is shown in Figure 4. From this result the ethylene polymerization is concluded to occur by the *cis*-opening process.[9]

In the case of the $Al(i\text{-}C_4H_9)_3$ catalyst, the infrared spectra of the prepared partially deuterated polyethylenes are different and they suggest some side reactions.[9,10]

This method of studying polymerization reaction has been applied by Miyazawa et al. to the case of polypropylene, and the *cis* opening process has again been found.[10]

Polyvinyl Chloride

The infrared spectra of various alkyl chlorides show C—Cl stretching bands in the region from 800 to 500 cm.$^{-1}$. The frequency of this C—Cl

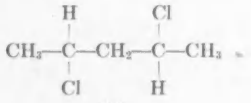
band is conformation-sensitive, and the observed frequency gives reliable information on the conformation of alkyl chloride molecule.[12–14]

The infrared spectra of poly(vinyl chloride) have been measured in this region, and the conformation and the tacticity have been studied with the use of the method referred to above.[12,15–17] Poly(vinyl chloride) prepared by the radiation polymerization in a urea canal complex has only two peaks at 638 and 603 cm.$^{-1}$ in this region. This result can only be explained by the fact that the molecule is syndiotactic and the conformation is the extended TTT form.*

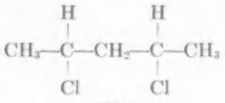
Ordinary poly(vinyl chloride) shows another isolated band at 690 cm.$^{-1}$ (S_C band) in addition to three or four bands appearing at 640–600 cm.$^{-1}$. This S_C band is assigned to the stretching vibration of the C—Cl bond located at the bent part of the main chain which is caused by the atactic or isotactic structure.

Poly(vinyl chloride) polymerized at low temperature has a weaker S_C band than that polymerized at high temperature, showing that the former is rich in the syndiotactic structure.

As model compounds of syndiotactic and isotactic poly(vinyl chloride), *d,l*- and *meso*-2,4-dichloropentane (I and II, respectively) have been prepared, the infrared spectra have been measured, and the conformations have been determined.[20]



(I)



(II)

The observed C—Cl stretching bands show that I has the TT conformation and II has the TG conformation with regard to the pentane chain.

The normal coordinate treatment has been made for the TTT structure of syndiotactic poly(vinyl chloride).[21] The frequencies were subsequently recalculated by use of the force constants, which can reproduce all the frequencies of simple alkyl chloride molecules including the C—Cl stretching frequencies.[22]

The results can explain all the frequencies observed for poly(vinyl chloride) polymerized at low temperature (Fig. 5). Frequencies have also been calculated for deuterated poly(vinyl chlorides). In Figure 5 they are

* The conformations of linear chain polymer molecules can be expressed by the consecutive arrangements of T (*trans* form) and G (*gauche* form).[18] When the right-handed and left-handed *gauche* forms are discriminated, the notations, G and G′, are used. All the conformations of linear polymers so far studied experimentally can be expressed by these basic structures or their slightly distorted forms.[19] Polyethylene, syndiotactic PVC, and syndiotactic and isotactic PVA are of the TTT form, polyoxymethylene is GGG, isotactic polypropylene and many other isotactic polymers are TGTG, poly(ethylene glycol) is TTG, the α- and ω-helices of polypeptides are TGG, and syndiotactic polypropylene, TTGG.

compared with those observed by Krimm et al.[23] The agreement with the observed frequencies is satisfactory for all of these compounds.

The frequencies of isotactic poly(vinyl chloride) have been calculated for the threefold helix TGTG conformation with the use of the same set of force constants.[22] The C—Cl frequencies calculated are located at 679

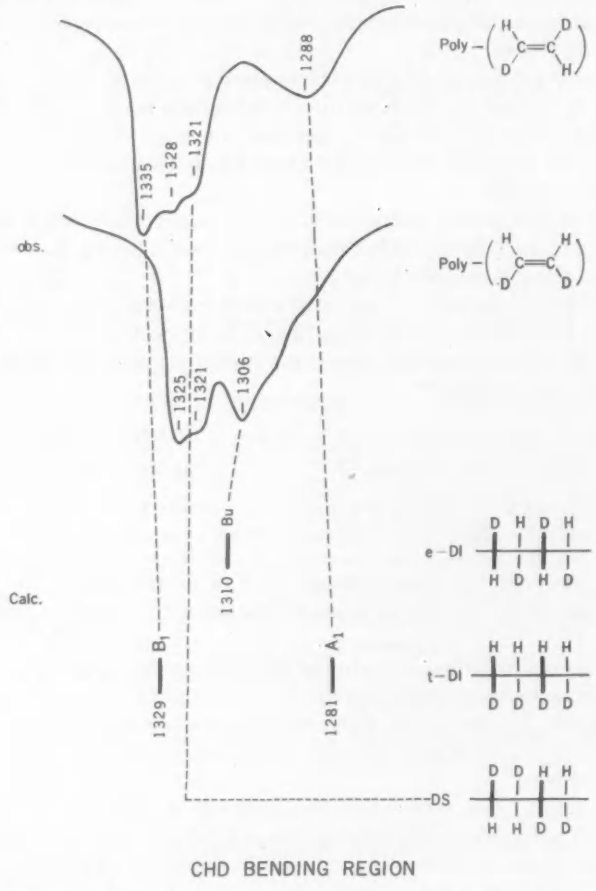


Fig. 4. Infrared spectra and calculated frequencies of polyethylenes $(CHD—CHD)_n$.[9]

cm.$^{-1}$ (A) and 675 cm.$^{-1}$ (E). These frequencies correspond very well to the observed bands at 690 and 683 cm.$^{-1}$ parallel and perpendicular to the direction of stretching, respectively (Fig. 6). This result does not deny the existence of atactic structures, since almost the same frequencies are expected for the C—Cl stretching vibrations. However, all the results ob-

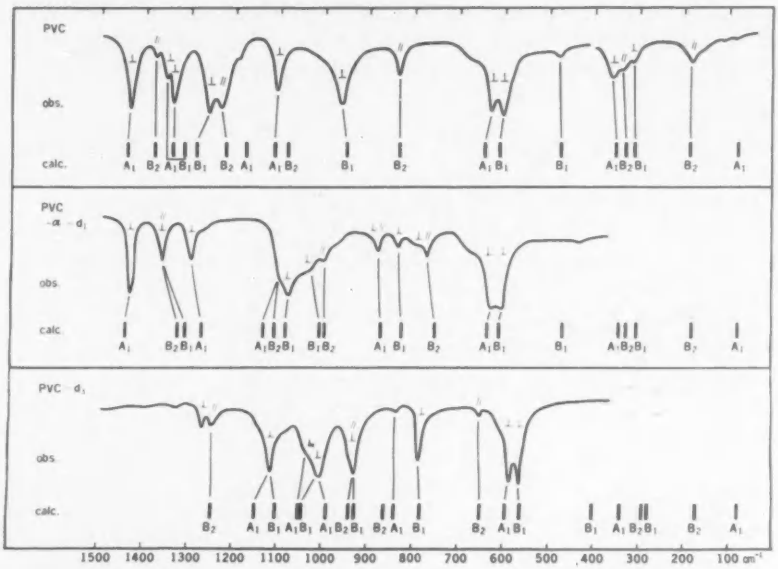


Fig. 5. Observed[22,23] and calculated frequencies of poly(vinyl chlorides).

tained for poly(vinyl chloride) and related compounds can be explained consistently by the frequency calculation.*

Infrared bands of poly(vinyl chloride) with the syndiotactic TTT structure can be classified into A_1, B_1, and B_2 species according to the symmetry properties.[21] The B_2 band has the direction of dipole change parallel to the main chain; the B_1 band has the direction of dipole change perpendicular to the CCC plane; the A_1 band has the direction of dipole change perpendicular to those of B_1 and B_2. The dichroism of these bands can give information on the molecular orientation in the extended polymer films.[25]

An extended film of PVC polymerized at high temperature and a fully extended film of PVC polymerized at low temperature show parallel dichroism for B_2 vibrations and perpendicular dichroism for B_1 and A_1 vibrations. This fact can be explained by the orientation of polymer molecules parallel to the direction of stretching. However, the partially extended film of PVC polymerized at low temperature shows a different dichroism,

* Recently Bovey measured the high resolution NMR spectra of PVC.[24] His results are not consistent with ours, because NMR spectra show that the tacticity of PVC polymerized at low temperature is not different from that of PVC polymerized at high temperature. The reason for this inconsistency is not clear. However, the effect of a difference in solubility may be a factor. The high resolution NMR spectra have been taken in chlorobenzene solution and the highly syndiotactic PVC is hardly soluble in ordinary solvents. The high resolution NMR spectra are very useful for tacticity studies. So far all other experimental results reported are consistent with the infrared results including those for the model compounds.

as seen in Figure 7. In this case, four B_1 vibrations appearing at 603, 957, 1254, and 1354 cm.$^{-1}$ show parallel dichroism. A probable explanation for this dichroism inversion phenomenon is the orientation of rodlike crystal-

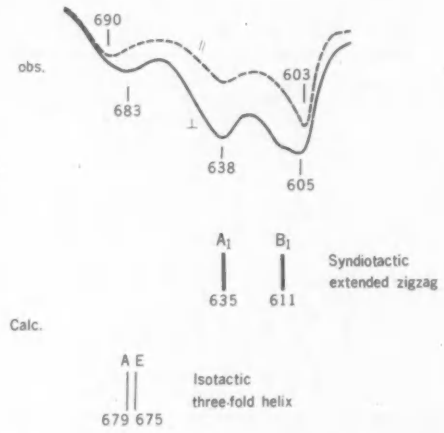


Fig. 6. C—Cl stretching region of infrared spectra of poly(vinyl chloride).

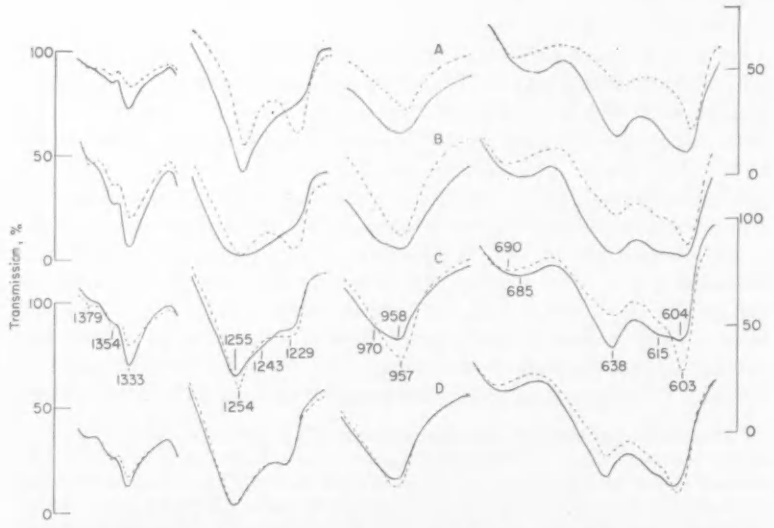


Fig. 7. Dichroism inversion in extended poly(vinyl chloride) film:[25] (——) electric vector perpendicular to draw direction; (- - -) electric vector parallel to draw direction; (*A*) draw ratio 7; (*B*) draw ratio 5; (*C*) draw ratio 2.5; (*D*) draw ratio 2; respectively. Numbers are frequencies in cm.$^{-1}$

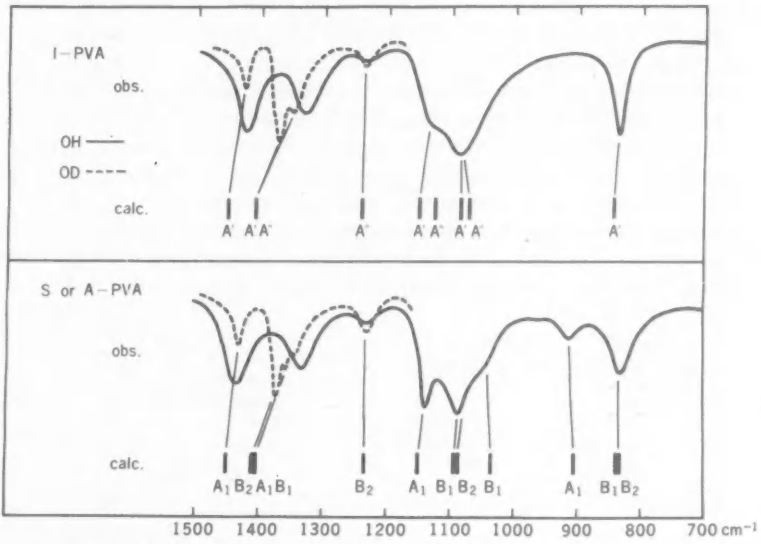


Fig. 8. Observed and calculated frequencies of isotactic and syndiotactic poly(vinyl alcohols).[28]

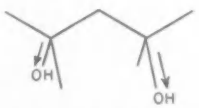


Fig. 9. Vibrational mode for A_1 band at 916 cm.$^{-1}$ of syndiotactic poly(vinyl alcohol).

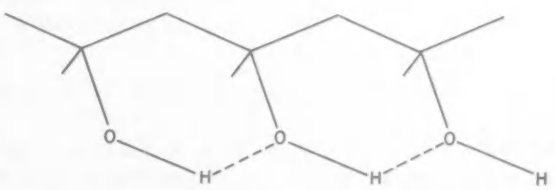


Fig. 10. Intramolecular hydrogen bond of isotactic poly(vinyl alcohol).

lites, in which the polymer chains are situated perpendicular to the direction of rod, in the initial stage of the extension of the film.[25,*]

Poly(vinyl Alcohol)

Isotactic poly(vinyl alcohol) has been prepared by Murahashi et al. and Fujii et al.[26,27] The infrared spectra of this polymer are different

* The perpendicular dichroism of B_2 bands, which is expected for the partially extended film, is probably not observed because of the overlap of the effect of molecular orientation parallel to the direction of stretching.

from those of ordinary, i.e., syndiotactic or/and atactic, poly(vinyl alcohol) as shown in Figure 8. The band observed at 916 cm.$^{-1}$ disappears, and the broad or doublet band at 849 and 835 cm.$^{-1}$ becomes a sharp singlet. X-ray diffraction study shows that isotactic poly(vinyl alcohol) takes the TTT form in the crystalline part just like the ordinary poly(vinyl alcohol).

The frequencies of normal vibrations have been calculated for the syndiotactic and isotactic poly(vinyl alcohol) in the TTT form, the OH group being treated as one dynamical unit.[28] Force constants have been transferred from those of simple alcohols.[29] The result of calculation is also shown in Figure 7. To avoid the effect of coupling with the OH bending vibration, the calculated frequencies are compared with the

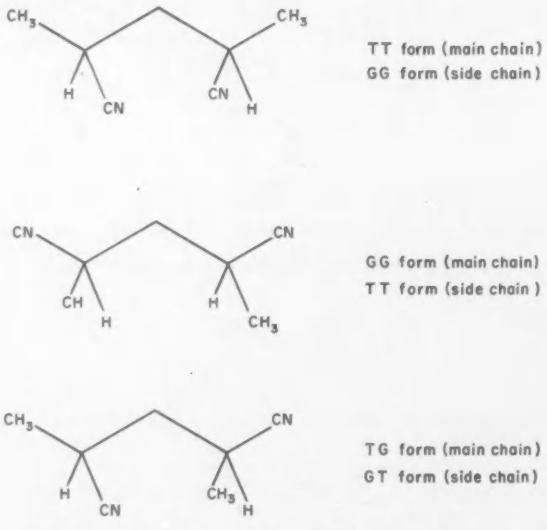


Fig. 11. Three stable forms of polyacrylonitrile model compounds.

spectra observed for $(CH_2—CHOD)_n$ in the 1500–1200 cm.$^{-1}$ region, which are given by dotted lines in the figure. The agreement between the observed and the calculated frequencies is also satisfactory.

The A_1 band at 916 cm.$^{-1}$ of the syndiotactic structure has the mode shown in Figure 9. This mode is strongly coupled with skeletal stretching vibrations and appears in this region. In the case of the isotactic polymer this coupling does not occur and no band is found in this region.

The fact that the isotactic poly(vinyl alcohol) molecules takes the TTT form can be understood by the existence of the intramolecular hydrogen bond shown in Figure 10.

The infrared spectra of *meso*-pentane-2,4-diol[30,31] and isotactic heptane-2,4,6-triol[31] show stable intramolecular hydrogen bonds in dilute carbon tetrachloride solutions.

Polyacrylonitrile

The tacticity of polyacrylonitrile has not yet been studied so extensively. It has not been correlated with the change in the infrared spectra. At the present stage the study of the model compounds seems to be important. We have studied the infrared spectra of *d,l-* and *meso*-2,4-dicyanopentane. With the use of the force constants obtained for the simple alkylcyanide molecules,[32] the normal frequencies have also been calculated for these molecules in the structures expected to be stable (Fig. 11). The comparison between the observed and the calculated frequencies show that the *meso*

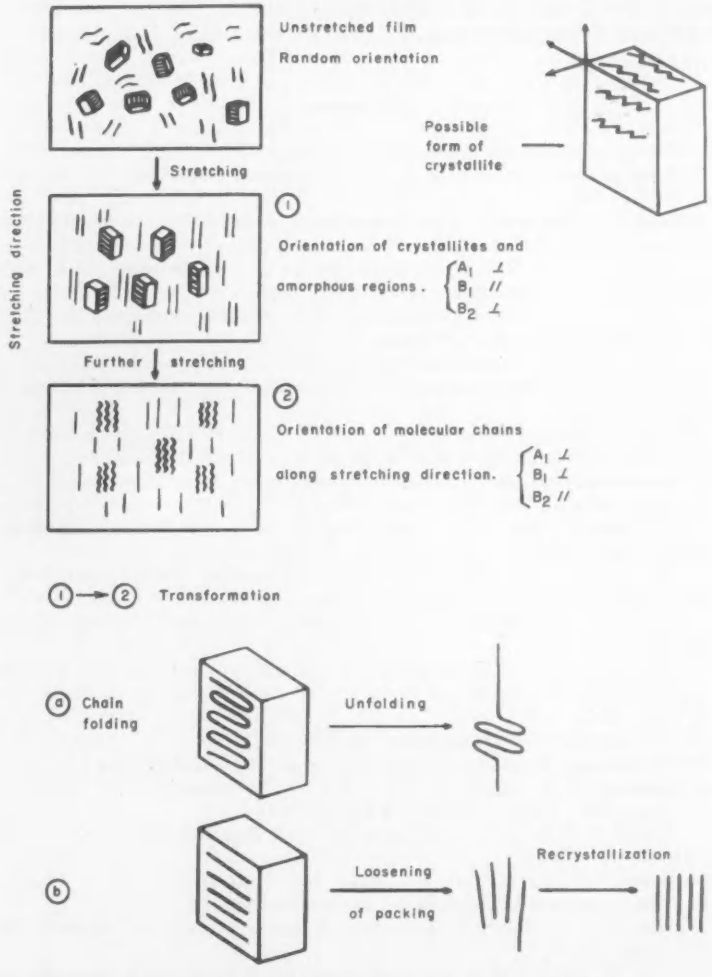


Fig. 12. Orientation of crystallites and polymer chains in PVC films.

isomer takes only the TG form and the *d,l* isomer takes both the TT and GG forms.[33] This result suggests that the isotactic polyacrylonitrile will take the TGTG threefold helix conformation and the syndiotactic polyacrylonitrile will take the TTT conformation, the TTGG conformation (as in the case of polypropylene), or a mixture of TTT and TTGG.

The reason why the *d,l*-2,4-dicyanopentane takes both the TT and GG forms and the *d,l*-2,4 dichloropentane takes only the TT form is ascribed to the dipole–dipole electrostatic interaction.[34] The C—CN bond has a larger dipole moment than the C—Cl bond. However, the fact that the center of dipole is closer to the main chain carbon atom for the C—Cl bond than for the C—CN bond explains the difference reasonably. This will explain also the conformation difference between poly(vinyl chloride) and polyacrylonitrile.

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Discussion

S. Krimm: (*University of Michigan, Ann Arbor, Michigan, U.S.A.*): I would like to ask Prof. Shimanouchi two questions. I am interested in the picture that you presented for folded chain crystals of PVC and how they orient and then unfold by stretching (Fig. 12). If this picture is correct, then it means that the parallel B_2 vibrations of poly(vinyl chloride) should show initial dichroism as you begin to stretch. They should begin to go perpendicular just as the B_1 vibrations begin to go parallel. Have you ever observed this with the B_2 vibrations?

T. Shimanouchi: One has to be very careful on this point. Electron diffraction studies on single crystals of PVC have shown that in the crystal the chain is perpendicular to the crystal long axis. Polarization measurements must be interpreted keeping these problems in mind. (See also the footnote in the text, p. 91.)

S. Krimm: You have shown the spectra of the model compounds *d,l*-2,4-dichloropentane in vapor, liquid and solid phases. If I recall, in the spectrum of the liquid there seem to be two additional very weak bands near 680 or 690 cm.$^{-1}$. If they are associated with the C—Cl stretching they would be the SHC bands. They could originate from the form 2 which you said is the less stable form.

Have you taken any spectra of the liquid as a function of temperature and measured the ratio of the intensities of these weak bands to the strong ones near 610–630 cm.$^{-1}$? Do those bands change? Do you think they might perhaps be due to a small amount of this form?

T. Shimanouchi: We have carried out careful measurements in the spectral region you have mentioned. If we have another form in the liquid state the amount of it should increase in the vapor phase. We did not find the band at 690 cm.$^{-1}$ in the spectrum of the vapors. The study of some other model compounds seems to me very important in order to solve the problem.

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Normal Coordinate Calculations of Large Hydrocarbon Molecules and Polymers

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I should like to start with our definition of a large molecule, namely, any molecule for which a normal coordinate calculation cannot conveniently be carried out on a desk calculator. This definition then includes propane, which is not a large molecule by some people's standards. We might ask why discuss "large" molecules which are as small as propane at a conference on the spectra of high polymers. The principal reason is that the spectra of small molecules are easier to assign. Thus, if one can assign the vibrational spectra of a series of molecules and evaluate a force field which can be demonstrated to transfer among the molecules of the series, this force field can then be used to calculate and assign the vibrational frequencies of related polymers with considerable confidence. From this point of view a polymer is just another large molecule. In addition, since the selection rules for regular infinite structures allow only a small number of active frequencies, it is difficult or impossible to evaluate a realistic force field from the spectra of the polymer itself.

We have evaluated an approximate valence force field for the fully extended normal paraffins including polyethylene and this has led to an assignment of polyethylene which is consistent with the observed and calculated spectra of the smaller normal paraffins. A second set of force constants has been evaluated from a series of branched paraffins and used to calculate and assign the vibrational frequencies of polypropylene.

Evaluation of Force Constants

Force constants were evaluated by a least-squares perturbation technique due to King, Crawford[1,2] and Shimanouchi.[3] By this procedure an initial trial set of force constants is refined by a first-order perturbation to give a least-squares fit of the calculated frequencies to the observed frequencies. Calculations were done on an IBM 7090 computer. Figure 1 gives a simplified schematic diagram of the computer program. The differences between the observed and calculated frequency parameters are related to the corrections in the force constants, $\Delta\Phi_j$, by the equation

$$\Delta\lambda_i = \sum_j J_{ij}\Delta\Phi_j \qquad (1)$$

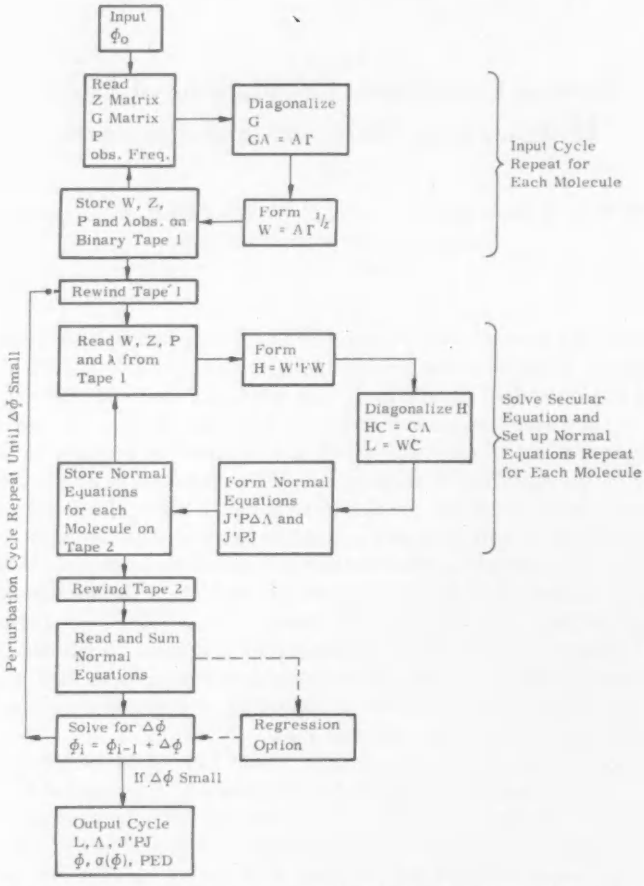

Fig. 1. Flow diagram for computer program for the least-squares adjustment of force constants.

King[1] has shown that the corrections to the initial $\boldsymbol{F}_0$ matrix are related to the frequency errors by

$$\Delta\lambda_t = \sum_k \sum_l (L_0)_{kt}(L_0)_{lt}\Delta F_{kl} \tag{2}$$

where the $(L_0)_{kt}$ are the elements of the normal coordinate transformation for the zero-th order secular equation

$$\boldsymbol{G}\boldsymbol{F}_0\boldsymbol{L}_0 = \boldsymbol{L}_0\Lambda_0 \tag{3}$$

Elements of the $\boldsymbol{F}$ matrix are related to the independent force constants Φ_j by a transformation Z[4]

$$F_{kl} = \sum_j Z_{klj}\,\Phi_j \tag{4}$$

The least-squares correction to the force constants is given by the solution of the set of linear equations

$$\boldsymbol{J'PJ\Delta\Phi} = \boldsymbol{J'P\Delta\Lambda} \tag{5}$$

where $\boldsymbol{P}$ is a diagonal weighting matrix. In our calculations we take $P_{ii} = 1/\lambda_i$. In the evaluation of a set of force constants for a series of molecules, the normal equations (5) for all of the molecules in the series are combined so that the final set of force constants gives the best possible fit to the observed frequencies of all the molecules considered and are by definition transferable within the series. The goodness of fit, then, gives a measure of the degree of transferability.

The normal equations are combined by summing the equations for the individual molecules, thus

$$\sum_m (\boldsymbol{J'PJ})_m \boldsymbol{\Delta\Phi} = \sum_m (\boldsymbol{J'P\Delta\Lambda})_m \tag{6}$$

In general, the number of vibrational frequencies is not sufficient to determine all of the force constants in the general harmonic force field, and one is faced with the job of choosing the most significant interaction constants. This can be done by trial and error, but if there are many possible interactions the number of combinations is very large and the process is time-consuming. In order to aid in the selection of interaction constants a stepwise multiple regression procedure has been coded into the least-squares perturbation program. The subroutine is a modification of the regression program coded by M. A. Efroymson[5] of the Esso Research and Engineering Company. By this procedure, interaction constants are added to the force field one at a time in the order which gives the greatest improvement in the fit between the observed and calculated frequencies as measured by the variance of λ: $V_\lambda = \sum_i P_{ii}(\Delta\lambda_i)^2$. This procedure is continued until the estimated standard error of the next force constant to be added becomes larger than the force constant itself. Provision is made for removing interaction constants which become uncertain through the addition of other interaction constants at each step in the regression. By this means a large number of interaction constants can be tested for significance in a single perturbation cycle.

Force Constants for the *n*-Paraffins and Polyethylene

The force constants used in the polyethylene calculation were evaluated by adjusting a set of 31 independent valence force constants to give a least-squares fit to 270 observed frequencies of a series of fully extended normal paraffins including crystalline polyethylene.[6] Torsional coordinates were included in the internal coordinates and the torsional force constant was estimated from the torsional frequency (280 cm.$^{-1}$) of ethane. Molecules included in the series were propane, *n*-butane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, and polyethylene. The final

TABLE I

Force Constants for the Normal Paraffins[a]

		Φ_i	$\sigma(\Phi_i)$	Example of coordinate or interaction (see Fig. 2)
1	$(CH_3)\ K_r$	4.704	0.003	1-4
2	$(CH_3)\ F_r$	0.039	0.002	1-4 with 2-4
3	$(CH_2)\ K_d$	4.546	0.004	7-5
4	F_d	0.016	0.004	7-5 with 8-5
5	$(CH_3—CH_3)\ K_R$	4.423	0.059	Ethane
6	$(CH_3—CH_2)\ K_R^{I}$	4.329	0.026	4-5
7	$(CH_2—CH_2)\ K_R^{II}$	4.427	0.042	5-6
8	F_R	0.064	0.030	4-5 with 5-6
9	$F_{R\gamma} = F_{R\beta}$	0.261	0.031	4-5 with 1-4-5
10	$F_{R\gamma}'$	−0.004	0.031	4-5 with 7-5-6
11	$F_{R\omega}$	0.351	0.022	4-5 with 4-5-6
12	$(CH_3)\ H_\alpha$	0.540	0.001	1-4-3
13	$(CH_2)\ H_\delta$	0.550	0.003	7-5-8
14	$(CH_3)\ H_\beta$	0.637	0.005	1-4-5
15	$(CH_3)\ F_\beta$	−0.017	0.005	1-4-5 with 2-4-5
16	$(CH_2)\ H_\gamma$	0.666	0.004	7-5-4
17	$(CH_2)\ F_\gamma$	−0.016	0.004	7-5-4 with 8-5-4
18	$(CH_2)\ F_\gamma'$	0.023	0.003	7-5-4 with 7-5-6
19	$(CH_2)\ F_{\gamma\omega}$	−0.124	0.039	7-5-4 with 4-5-6
20	H_ω	0.901	0.059	4-5-6
21	f_ω^{t}	0.093	0.021	4-5-6 with 5-6-9
22	$f_{\beta\omega}^{t} = f_{\gamma\omega}^{t}$	0.072	0.011	1-4-5 with 4-5-6
23	$f_{\beta\omega}^{g} = f_{\gamma\omega}^{g}$	−0.058	0.008	7-5-6 with 5-6-9
24	$f_\beta^{t} = f_{\beta\gamma}^{t} = f_\gamma^{t}$	0.106	0.006	3-4-5 with 4-5-7
25	$f_\beta^{g} = f_{\beta\gamma}^{g} = f_\gamma^{g}$	−0.024	0.006	3-4-5 with 4-5-8
26	$f_{\beta\gamma'}^{t} = f_{\gamma'}^{t}$	−0.002	0.001	2-4-5 with 7-5-6
27	$f_{\beta\gamma'}^{g} = f_{\gamma'}^{g}$	0.002	0.001	2-4-5 with 8-5-6
28	$f_{\gamma''}^{t}$	−0.001	0.006	8-5-4 with 10-6-9
29	$f_{\gamma''}^{g}$	0.001	0.006	8-5-4 with 11-6-9
30	$h_{\beta\gamma}^{c} = h_\gamma^{c}$	−0.002	0.003	2-4-5 with 10-6-5
31	$h_{\beta\gamma}^{c} = h_\gamma^{c}$	−0.003	0.002	2-4-5 with 11-6-5
32	H_τ	0.008	—	Torsion about 4-5

[a] Stretching constants in units of mdyne/A., stretch-bend interaction constants in units of mdyne/rad., and bending constants in units of mdyne-A./rad.^{2}.

converged set of force constants given in Table I reproduced the observed frequencies with an average error of 0.29% or about 3.5 cm.$^{-1}$. The largest error was 15 cm.$^{-1}$. A complete tabulation of the calculated and observed frequencies has been given elsewhere.[6]

The approximate valence force field given in Table I contains 11 diagonal force constants including the torsional constant H_τ. The CH_3 group and the CH_2 group were given different diagonal force constants. Important interactions include $F_{R\beta} = F_{R\gamma}$, an interaction between a CC stretch and an HCC bend with a C—C bond in common; $F_{R\omega}$ a CC stretch–CCC bend

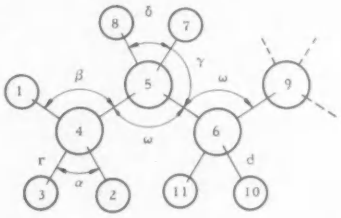

Fig. 2. Internal coordinates for normal paraffins.

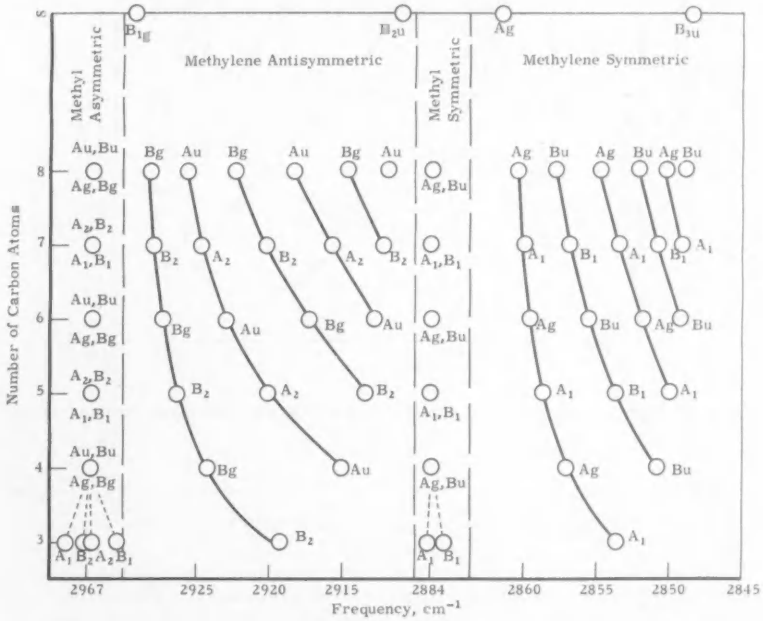

Fig. 3. Calculated frequencies of methyl and methylene C—H stretching modes.

interaction with a C—C bond in common; F_β and F_γ, ∠HCC–∠HCC interactions with a C—C bond in common and with H atoms bonded to the same carbon atom for a CH_3 group and a CH_2 group respectively; F_γ' and ∠HCC–∠HCC interaction with a CH bond in common; $F_{\gamma\omega}$ and ∠HCC–∠CCC interaction with a C—C bond in common, and the *trans* and *gauche* bending interaction constants f_ω^t, $f_{\gamma\omega}^t$, $f_{\gamma\omega}^g$, f_γ^t, and f_γ^g.

Results of these calculations are presented in Figures 3–7 and 11–13. The CH stretching modes are given in Figure 3 and we see that the limiting frequencies for the infinite chain are at 2931 cm.$^{-1}$ (B_{1g}) and 2913 cm.$^{-1}$ (B_{2u}) for the antisymmetric CH_2 stretch and at 2864 cm.$^{-1}$ (A_g) and 2851 cm.$^{-1}$ (B_{3u}) for the symmetric CH_2 stretching modes. Figure 4 gives the

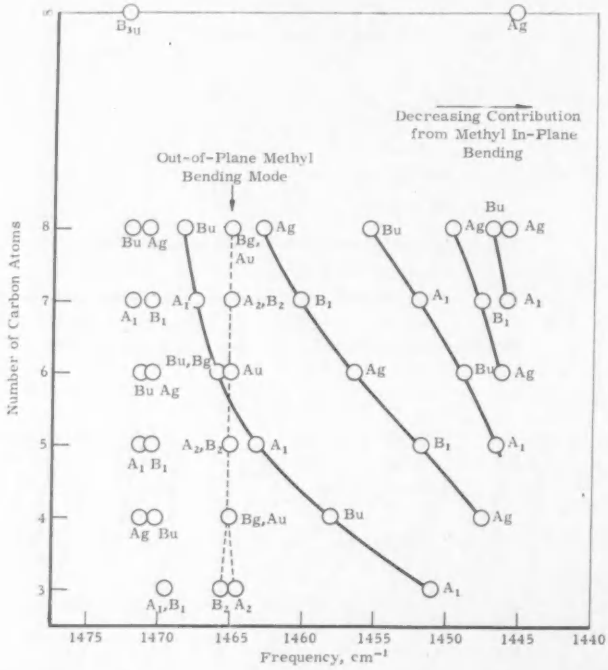

Fig. 4. Calculated frequencies of methyl asymmetric and methylene bending modes

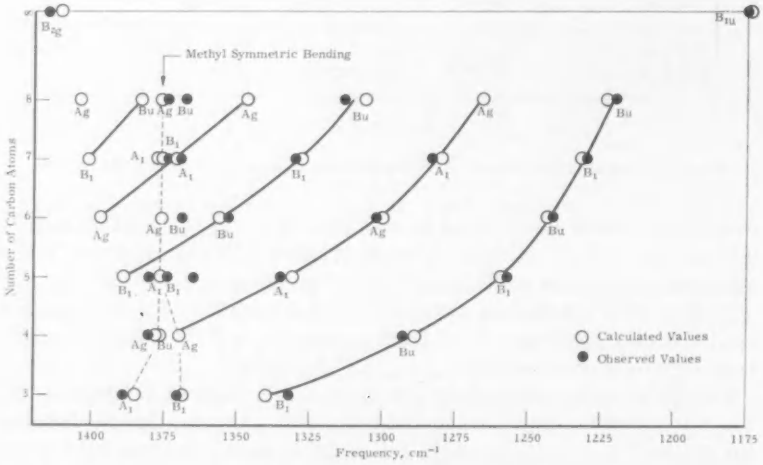

Fig. 5. Calculated and observed frequencies of methylene wagging and methyl symmetric bending modes.

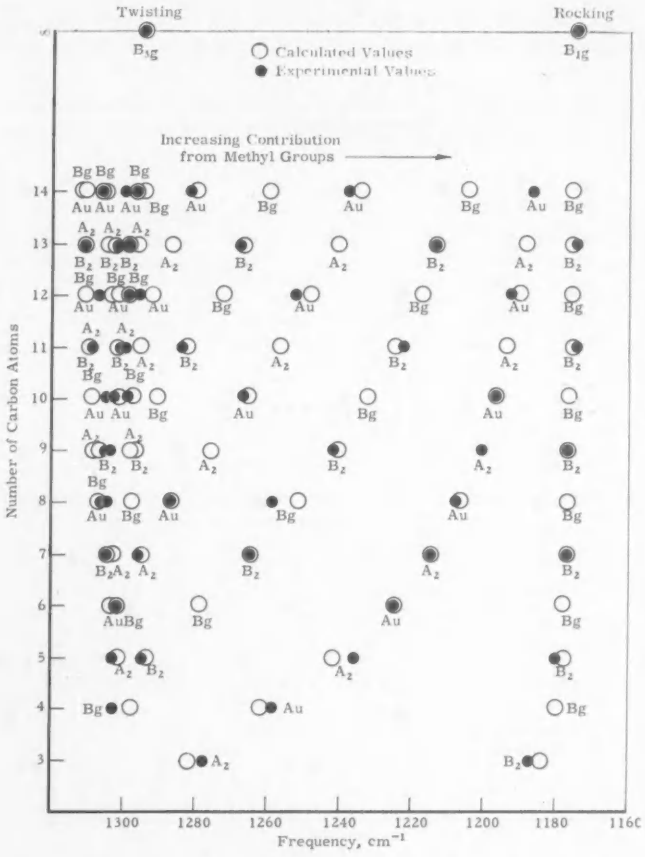

Fig. 6. Calculated and observed frequencies of the methylene twisting-rocking region (1310–1175 cm.$^{-1}$).

CH_3 and CH_2, HCH bending modes with the limiting frequencies at 1474 cm.$^{-1}$ (B_{3u}) and 1445 cm.$^{-1}$ (A_g) for the CH_2 bending modes of polyethylene. Normal coordinates for the bending modes in molecules of finite length show a considerable coupling between the CH_3 bending mode and the CH_2 bending mode. The limiting frequencies for the CH_2 wagging modes in Figure 5 are at 1413 cm.$^{-1}$ (B_{2g}) and 1170 cm.$^{-1}$ (B_{1u}). The CH_2 twisting and rocking motions couple to form two series of bands, a high frequency series with limiting frequencies of 1295 cm.$^{-1}$ (B_{3g}) and 1175 cm.$^{-1}$ (B_1), and a low frequency series with limiting frequencies of 1061 cm.$^{-1}$ (A_u) and 721 cm.$^{-1}$. The series are plotted in Figures 6 and 7. Vibrations with frequencies near 1295 and 1061 cm.$^{-1}$ are almost pure CH_2 twisting modes and vibrations with frequencies near 1170 and 721 cm.$^{-1}$

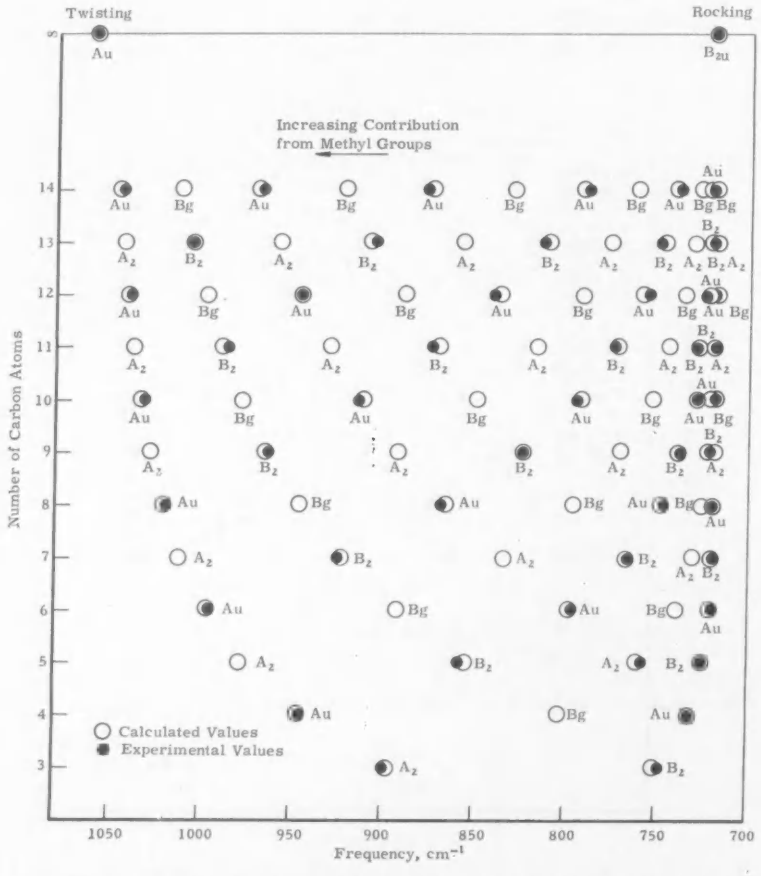

Fig. 7. Calculated and observed frequencies of the methylene twisting-rocking region (1060–720 cm.$^{-1}$).

are almost pure CH_2 rocking modes. Intermediate frequencies are mixtures of twist and rock. Figures 8–10 illustrate the forms of the limiting modes and some intermediate frequencies in n-$C_{20}H_{42}$. The length of the arrow on each atom is proportional to the L's for the twist or rock centered on the atom. In molecules of finite length the out-of-plane CH_2 rocking motion mixes with the CH_2 rock and twist and becomes part of the series. The CCC bending array is given in Figure 11 and the limiting frequencies are 0. There is a maximum in the array at about 535 cm.$^{-1}$. The C—C stretching array is plotted in Figure 12. Limiting frequencies for the C—C stretch array are at 1133 cm.$^{-1}$ (A_g) and 1063 cm.$^{-1}$ (B_{2g}) with a minimum in the phase frequency curve at 970 cm.$^{-1}$. Table II summarizes the assignments for polyethylene. Tasumi, Shimanouchi, and Miyazawa[7]

have recently calculated the vibrational frequencies of polyethylene with the Urey-Bradley force field, and their assignments are in agreement with ours.

In molecules of finite length, the in-plane CH_3 rock mixes strongly with the terminal C—C stretch to form the array given by Figure 13. The very

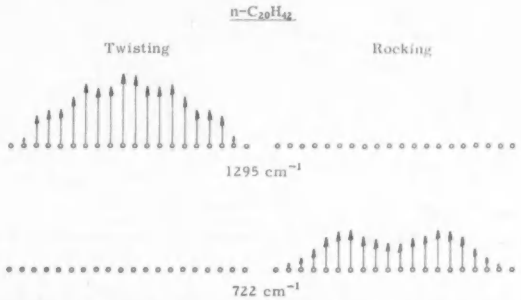

Fig. 8. In-phase ($\varphi = 0$) twisting and rocking modes for n-$C_{20}H_{42}$. Lengths of arrows are proportional to L's.

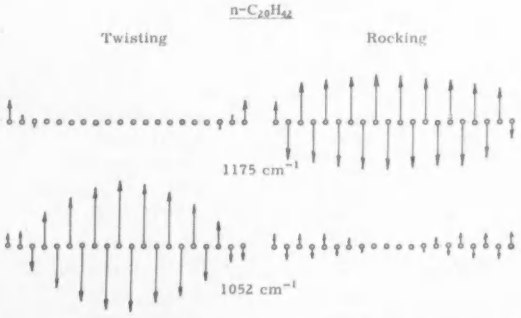

Fig. 9. Out-of-phase ($\varphi = \pi$) twisting and rocking modes for n-$C_{20}N_{42}$. Lengths of arrows are proportional to L's.

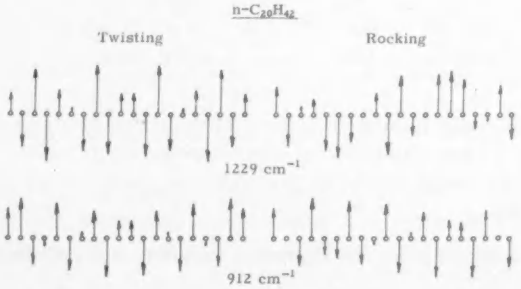

Fig. 10. Mixed twisting-rocking modes ($\varphi = \pi/2$) for n-$C_{20}H_{42}$. Lengths of arrows are proportional to L's.

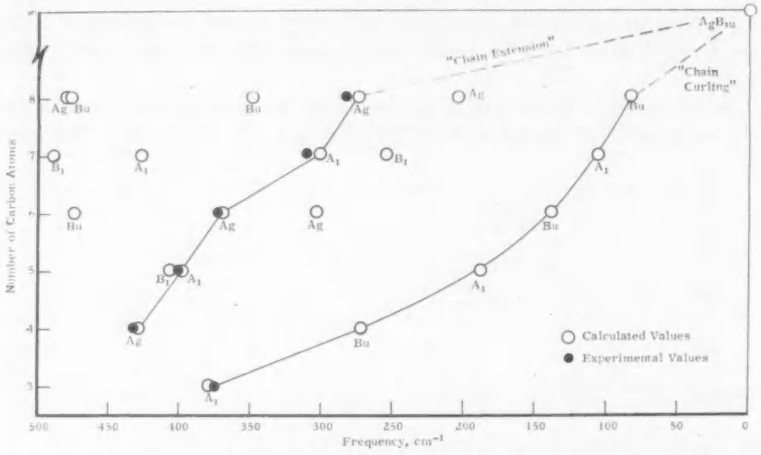

Fig. 11. Calculated and experimental frequencies of ∠CCC bending modes.

TABLE II

Polyethylene Assignments

	Frequency $cm.^{-1}$		
	Obs.	Calc.	Description
A_g	2865	2864	d^+ (C—H stretch)
	1440	1440	δ (CH_2 bend)
	1133	1133	R (C—C stretch)
B_{1g}	2932	2931	d^- (C—H stretch)
	1174	1172	P (CH_2 rock)
B_{2g}	1415	1410	W (CH_2 wag)
	1065	1057	R (C—C stretch)
B_{2g}	1295	1295	T (CH_2 twist)
A_u	1063	1061	T (CH_2 twist)
B_{1u}	1170	1169	W (CH_2 wag)
B_{2u}	2919	2913	d^- (C—H stretch)
	722	718	P (CH_2 rock)
B_{2u}	2851	2851	d^+ (C—H stretch)
	1475	1469	δ (CH_2 bend)

good fit to this large number of observed frequencies is an indication of the high degree of transferability of the force constants given in Table I. Encouraged by these results we proceeded to the branched paraffins and polypropylene.

Force Constants for the Branched Paraffins and Polypropylene

In order to calculate the spectra of polypropylene the force field used for the normal paraffins was modified to include all saturated hydrocarbons.

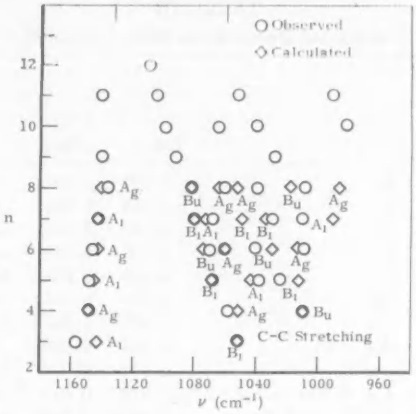

Fig. 12. Calculated and observed frequencies of the C—C stretching modes.

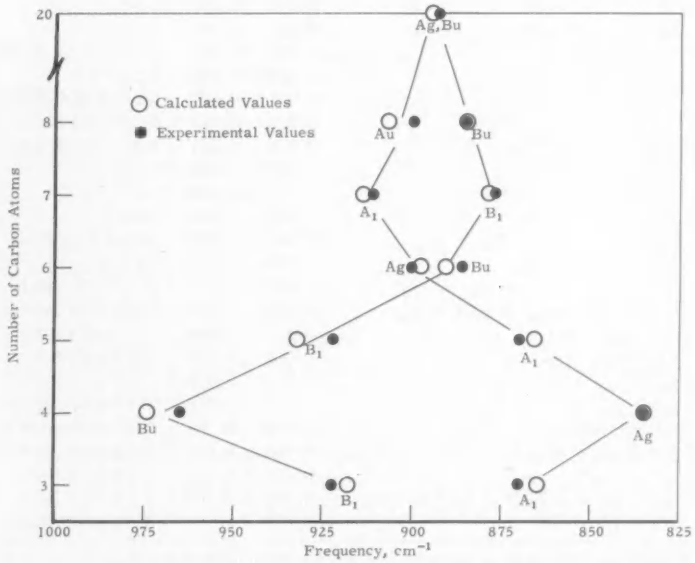

Fig. 13. Calculated and experimental frequencies of the in-plane methyl rocking mode.

The force field was modified by dropping the interaction constants $h_\gamma{}^e$ and $h_\gamma{}^c$ and by adding six new constants. Constants added were K_s and H_t, a CH stretching constant and an HCC bending constant for a tertiary H atom, e.g., $HC(CH_2)_3$; H_φ a CCC bending constant for an $HC(C_3)$ group; $F_{\varphi\varphi}$ an $\angle CCC$–$\angle CCC$ interaction with a C—C bond in common; H_Δ, a CCC bending constant for a $C(C)_4$ group; and $f_\omega{}^g = f_{\omega\varphi}{}^g = f_{\varphi\Delta}{}^g$, a *gauche*

TABLE III

Saturated Hydrocarbon Force Constants[a]

		Φ_i	$\sigma(\Phi_i)$	Example of coordinate or interaction (see Fig. 14)
1	K_r	4.699	0.008	11-10
2	F_r	0.043	0.006	11-10 with 12-10
3	K_d	4.554	0.010	5-2
4	F_d	0.006	0.010	5-2 with 6-2
5	K_s	4.588	0.036	9-3
6	K_R	4.387	0.035	10-3
7	K_S	4.337	0.047	2-3
8	K_T	4.534	0.225	
9	$F_R = F_{RS} = F_S = F_T$	0.101	0.016	2-3 with 10-3
10	$F_{R\xi} = F_{R\beta} = F_{S\gamma} = F_{S\xi} = F_{T\zeta}$	0.328	0.015	2-3 with 2-3-9
11	$F_{R\varphi} = F_{S\omega} = F_{S\varphi} = F_{T\Lambda}$	0.417	0.019	2-3 with 2-3-4
12	$F_{R\xi}' = F_{S\gamma}' = F_{S\xi}'$	0.079	0.015	2-3 with 9-3-4
13	H_α	0.540	0.002	11-10-12
14	H_δ	0.550	0.005	7-4-8
15	H_β	0.645	0.004	11-10-3
16	F_β	−0.012	0.003	11-10-3 with 12-10-3
17	H_γ	0.656	0.004	5-2-3
18	F_γ	−0.021	0.004	5-2-3 with 6-2-3
19	$F_\gamma' = F_\zeta'$	0.013	0.004	5-2-3 with 5-3-1
20	$F_{\gamma\omega} = F_{\zeta\varphi} = F_{\zeta\Lambda}$	−0.031	0.017	5-2-3 with 1-2-3
21	H_ζ	0.657	0.008	9-3-4
22	H_ω	1.130	0.039	1-2-3
23	H_φ	1.084	0.038	4-3-10
24	$F_\varphi = F_\Lambda$	−0.041	0.023	4-3-10 with 2-3-4
25	H_Λ	1.086	0.027	14-1-15
26	$f_{\gamma\omega}{}^t = f_{\gamma\varphi}{}^t = f_{\beta\varphi}{}^t = f_{\zeta\varphi}{}^t = f_{\zeta\omega}{}^t$	0.049	0.011	8-4-3 with 2-3-4
27	$f_{\gamma\omega}{}^\theta = f_{\gamma\varphi}{}^\theta = f_{\beta\varphi}{}^\theta = f_{\zeta\varphi}{}^\theta = f_{\zeta\omega}{}^\theta$	−0.052	0.010	7-4-3 with 2-3-4
28	$f_\gamma{}^t = f_{\gamma\xi}{}^t = f_{\beta\gamma}{}^t = f_{\beta\zeta}{}^t$	0.127	0.006	5-2-3 with 9-3-2
29	$f_\gamma{}^\theta = f_{\gamma\xi}{}^\theta = f_{\beta\gamma}{}^\theta = f_{\beta\zeta}{}^\theta$	−0.005	0.005	6-2-3 with 9-3-2
30	$f_\omega{}^t = f_{\omega\varphi}{}^t = f_\varphi{}^t = f_{\omega\Lambda}{}^t = f_\Lambda{}^t$	−0.011	0.029	1-2-3 with 2-3-4
31	$f_\omega{}^\theta = f_{\omega\varphi}{}^\theta = f_\varphi{}^\theta = f_{\omega\Lambda}{}^\theta = f_\Lambda{}^\theta$	0.011	0.016	1-2-3 with 2-3-10
32	$f_\gamma{}'{}^t = f_{\beta\gamma}{}'{}^t = f_{\beta\zeta}{}'{}^t = f_{\gamma\xi}{}'{}^t = f_\xi{}'{}^t$	0.002	0.004	9-3-2 with 6-2-1
33	$f_\gamma{}'{}^\theta = f_{\beta\gamma}{}'{}^\theta = f_{\beta\zeta}{}'{}^\theta = f_{\gamma\xi}{}'{}^\theta = f_\xi{}'{}^\theta$	0.009	0.004	9-3-2 with 5-2-1
34	$f_\gamma{}''{}^t = f_{\beta\gamma}{}''{}^t = f_{\beta\zeta}{}''{}^t = f_{\gamma\xi}{}''{}^t = f_\xi{}'{}^t$	−0.014	0.008	9-3-4 with 6-2-1
35	$f_\gamma{}''{}^\theta = f_{\beta\gamma}{}''{}^\theta = f_{\beta\zeta}{}''{}^\theta = f_{\gamma\xi}{}''{}^\theta = f_\xi{}''{}^\theta$	−0.026	0.007	9-3-4 with 5-2-1
36	$H_\gamma = H_\tau = H_\theta$	0.008	..	Torsion about 2-3

[a] Stretching constants in units of mdyne/A., stretch-bend interaction constants in units of mdyne/rad., and bending constants in units of mdyne-A. (rad.)^2.

∠CCC–∠CCC interaction. Three types of C—C stretching constants were included, K_R for C—C bonds with a total of four or five H's bonded to the carbons, K_S for bonds with a total of two or three H's bonded to the carbons, and K_T for bonds with a total of zero or one H bonded to the carbons. Force constants from the normal paraffins and from isobutane and neopentane[6] were used to calculate and assign the vibrational fre-

TABLE IV

Observed and Calculated Infrared-Active Frequencies

	Frequency, cm.$^{-1}$		Frequency, cm.$^{-1}$	
	Obs.	Calc.	Obs.	Calc.
	A Block		*B* Block	
gauche-n-Butane		1379		1377
		1355		1342
	1282	1271		1254
	1167	1172	1133	1123
	1077	1072	956	963
	981	989		948
	835	835	747	748
	789	798		469
		325		
	A_u Block		B_u Block	
2,3-Dimethylbutane	1368	1370	1377	1372
	1304	1317	1278	1274
	1067	1095	1155	1158
	956	974	871	874
	918	920		417
	E Block		F_2 Block	
Adamantane		1344	1452	1459
	1222	1218	1354	1351
		912	1289	1284
	442	427	1101	1108
			966	966
			800	795
			632	648
				397

quencies *gauche-n*-butane, *gauche-n*-pentane, isopentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2,2,3-trimethylbutane, 2,2,3,3-tetramethylbutane, cyclohexane, κ-methylcyclohexane, 1,1-dimethylcyclohexane, adamantane, and *trans*-decalin.

This modified force field was then refined to fit 308 observed frequencies of the molecules listed above and of propane, extended *n*-butane, extended

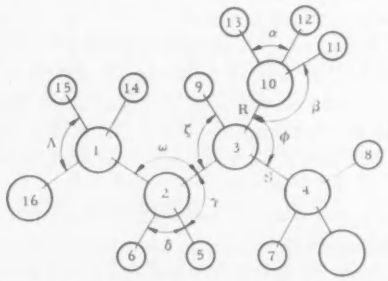

Fig. 14. Internal coordinates for branched paraffins.

n-pentane, isobutane, and neopentane. A total of 35 constants was adjusted and the torsional constant for rotation about the C—C bond was estimated from the ethane barrier and was assumed to be equal for all types of C—C bonds. The converged set of force constants is given in Table III, along with the estimated dispersions, $\sigma(\Phi_i)$. Agreement between observed and calculated frequencies was an average of 0.95% or 7.8 cm.$^{-1}$ (227 frequencies agreed to within 10 cm.$^{-1}$). To give you some idea of the agreement the observed and calculated frequencies of *gauche-n*-butane, 2,3-dimethylbutane, and adamantane are given in Table IV. These force constants have been used to calculate and assign the vibrational frequencies of crystalline isotactic polypropylene and to predict the vibrational frequencies of the two most probable forms of crystalline syndiotactic polypropylene.

The structure of crystalline isotactic polypropylene has been reported by Natta et al.[8] The structure is a helical chain.

A general method for treating the normal vibrations of infinite helical molecules by the $\boldsymbol{G}$ matrix method has been developed by Higgs.[9] The infinite $\boldsymbol{G}$ and $\boldsymbol{F}$ matrices are factored into the finite matrices $\boldsymbol{G}(\delta)$ and $\boldsymbol{F}(\delta)$ which are a function of the phase difference δ between adjacent units in the chain. The order of $\boldsymbol{G}(\delta)$ and $\boldsymbol{F}(\delta)$ is equal to the number of internal coordinates per monomer unit, but the elements are complex. Recently Miyazawa[10] and Tadokoro[11] have developed a procedure for obtaining $\boldsymbol{G}(\delta)$ and $\boldsymbol{F}(\delta)$ with real symmetry coordinates. Miyazawa[13] has applied this method to calculate the vibrational frequencies of isotactic polypropylene with the Urey-Bradley force field.

However if we restrict ourselves to the vibrational modes which retain translational symmetry we can use the same method on helical polymers that has been used on zigzag polymers such as polyethylene.[12] In this case we must consider the entire translational repeat unit, i.e., the smallest unit of the chain which can be transformed into an identical unit by a simple translation. Our existing computer programs for molecules were easily adapted to this latter method.

The translational repeat unit of the isotactic polypropylene chain contains three monomer units related to each other by a three-fold helix axis. The formulation of the $\boldsymbol{G}$ matrix and the $\boldsymbol{F}$ matrix can be carried out as if the repeat unit were a single molecule, but under the condition that the head and tail of the repeat unit be coupled in phase. The secular equation for the $3N$-4 modes of the repeat unit can be factored under the point group which is isomorphous with the infinite factor group of the chain. For crystalline isotactic polypropylene the 77 modes are classified under the point group C_3 into 25 parallel modes (A) and 52 perpendicular modes (E).

The symmetrized $\mathcal{G}$ and $\mathcal{F}$ matrices for the repeat unit can be generated by the following transformations

$$\mathcal{G} = \boldsymbol{U}_2\boldsymbol{G}\boldsymbol{U}_1'$$

and

$$\mathfrak{F} = \boldsymbol{U}_2\boldsymbol{F}\boldsymbol{U}_1'$$

$\boldsymbol{U}_1$ is the transformation which generates the 90 symmetry coordinates of the chain from the 90 internal coordinates, $\boldsymbol{R}_1$, of the repeat unit.* $\boldsymbol{U}_2$ defines a second set of 90 symmetry coordinates which are generated from another set of internal coordinates, $\boldsymbol{R}_2$, which includes the 90 coordinates of the repeat unit plus all other internal coordinates which have non-zero interactions with the internal coordinates of the repeat unit in the unsymmetrized $\boldsymbol{G}$ or $\boldsymbol{F}$ matrix for the infinite chain. For isotactic polypropylene

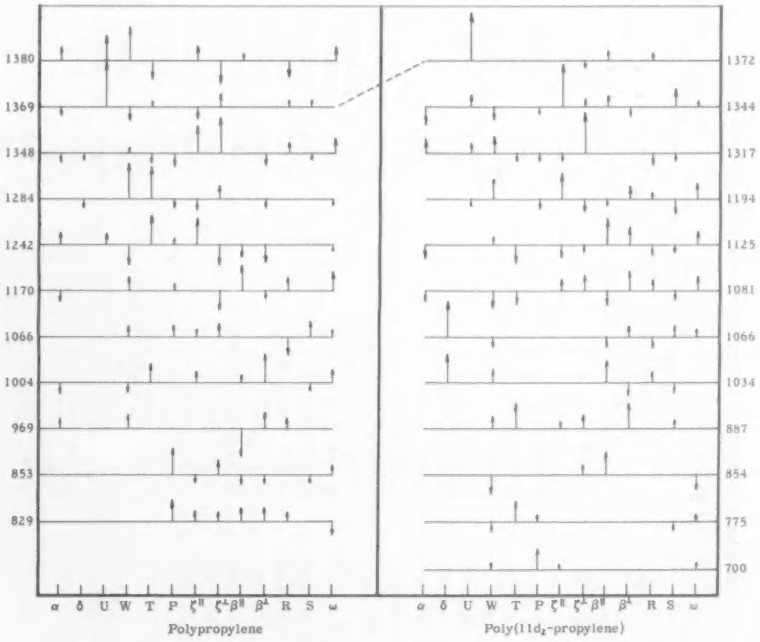

Fig. 15. Normal coordinates. Lengths of arrows are proportional to L.

our force field required 143 coordinates in $\boldsymbol{R}_2$. The dimensions of $\boldsymbol{G}$ and $\boldsymbol{F}$ are therefore 143 by 90. It is possible to factor the problem into three secular equations of order thirty, however, this requires a complex $\boldsymbol{U}_1$ and $\boldsymbol{U}_2$ and leads to a Hermitian $\mathfrak{G}$ and $\mathfrak{F}$ matrix and complex eigenvectors. To avoid this complication we left the E block unfactored. The $\boldsymbol{G}$ matrix was set up and transformed with an IBM 7090 computer program which will handle up to 400 internal coordinates.

* There are 90 internal coordinates for the three monomer units, and there are a total of 13 redundancies, nine from the redundancy among the six valence angles about each carbon atom and four which preserve the length and shape of the repeating unit.

TABLE V

Frequencies ν of Isotactic Polypropylene and Deuterated Analogs

Polymer	*A* Block			*E* Block		
	ν_{Calc}, cm.$^{-1}$	ν_{Obs}, cm.$^{-1}$[a,b]	Approx. potential energy distribution, %[c]	ν_{Calc}, cm.$^{-1}$	ν_{Obs}, cm.$^{-1}$[a,d]	Approx. potential energy distribution, %[c]
Polypropylene[e]	2962	2956(s)	r^-(100)	2962	2956	r^-(100)
	2962		r^{1-}	2962	2951(s)	r^-(100)
	2828		d^-(99)	2930	2925(sh)	d^-(94)
	2906		s(98)	2904	2907(sh)	s(94)
	2883		r^+(98)	2882	2880(s)	r^+(98)
	2855	2843(s)	d^+(99)	2856	2868(s)	d^+(99)
	1465		α(78)	1463	1459(sh)	α(88)
	1461		α(87)	1462		α(78)
	1453	1454(s)	δ(69, α(11)	1454		δ(69)
	1380	1378(m)[f]	W(27), S(26), ζ(25), U(20)	1377	1377(s)	U(38), W(21), ζ(21), S(16)
	1369	1365(vw)[f]	U(89)	1367	1359(m)	U(69), ζ(19)
	1348		ζ(65), S(12)	1352	1329(w)	ζ(52), T(15)
	1284	1305(w)	W(37), T(36)	1292	1297(w)	W(35), ζ(25), T(13)
	1242	1257(w)	ζ(37), T(19), β(15)	1201	1219(w)	T(26), ζ(20), R(19)
	1170	1167(s)	S(30), β(22)	1155	1153(sh)	S(23), R(15), ζ(13), β(13)
	1066	1044(w)	R(51), S(31)	1121	1103(w)	R(32), β(24), ζ(16)
	1004	997(s)	β(46), ζ(19)	1024		S(30), R(18), ζ(15), T(14)
	969	973(s)	β(51), S(28)	940	941(w)	β(45), R(40)
	853	841(s)	P(43), R(23)	901	900(w)	β(49), P(17), ζ(17)
	829		P(29), S(32), β(20)	817	809(m)	R(32), P(30), S(23)
	456	456[f]	ω(81)	513	528[f]	ω(63), R(10), P(9)
	392	398[f]	ω(62), ζ(15)	429	408[g,h]	ω(58), ζ(29), P(17)
	267		ω(58), τ(15)	311	321[f]	ω(74)
	195		τ(88)	198		τ(94)
	140		ω(50), τ(30)	147		ω(77), τ(16)
				63		τ(86)

Polypropylene-3,3,3-d_3[1]	2928	2918(vs)	$d^-(99)$	2930		$d^-(94)$
	2906	2907(s)	$s(98)$	2904		$s(94)$
	2855	2838(s)	$d^+(99)$	2856	2837(s)	$d^+(99)$
	2213		$r^-(98)$	2213	2204(s)	$r^-(98)$
	2213		$r^-(98)$	2213		$r^-(98)$
	2076	2066(m)	$r^+(97)$	2076	2067(m)	$r^+(98)$
	1454	1440(m)	$\alpha(77)$	1455	1438(m)	$\delta(77)$
	1376	1379(w)	$\zeta(35)$, $S(35)$, $W(30)$	1368	1361(s)	$\zeta(39)$, $W(27)$, $S(24)$
	1343	1334(w)	$\zeta(65)$	1348	1333(m)	$\zeta(51)$, $T(15)$, $W(13)$
	1283	1288(m)	$T(36)$, $W(37)$	1280	1297(m)	$\zeta(38)$, $W(36)$
	1215	1239(s)	$\zeta(51)$, $T(25)$	1184	1206(w)	$T(29)$, $\zeta(27)$, $S(21)$
	1138		$S(47)$, $\zeta(10)$, $W(10)$	1131	1144(s)	$S(19)$, $R(17)$, $P(13)$
	1085		$R(50)$, $U(40)$	1089	1081(m)	$R(56)$, $\zeta(11)$, $U(10)$
	1052	1051(vs)	$\alpha(89)$	1063	1054(vs)	$U(75)$, $S(24)$
	1049		$\alpha(96)$	1048		$\alpha(93)$
	1015	989(w)	$U(55)$, $S(24)$	1047		$\alpha(88)$
	932	908(w)	$R(20)$, $S(16)$, $\beta(15)$, $T(10)$	984	984(w)	$S(20)$, $R(13)$, $P(12)$, $\beta(11)$
	835	807(w)	$P(64)$, $R(13)$	821	821(m)	$R(20)$, $P(18)$, $S(17)$, $\beta(17)$
	794	791(s)	$\beta(67)$	758	759(m)	$\beta(61)$, $P(15)$, $S(13)$
	710	703(m)	$\beta(67)$, $S(19)$	738	743(w)	$\beta(62)$, $S(14)$
	422		$\omega(73)$, $\beta(13)$	488		$\omega(57)$, $S(10)$, $\beta(10)$
	357		$\omega(62)$, $\beta(16)$	402		$\omega(55)$, $\zeta(27)$
	256		$\omega(56)$, $\zeta(12)$, $\tau(12)$	285		$\omega(74)$
	145		$\tau(65)$, $\omega(27)$	147		$\tau(62)$, $\omega(34)$
	125		$\tau(51)$, $\omega(33)$	128		$\tau(50)$, $\omega(45)$
				58		$\tau(86)$

(continued)

TABLE V (*continued*)

Polymer	*A* Block			*E* Block		
	ν_{Calc}, cm.$^{-1}$	ν_{Obs}, cm.$^{-1}$[a,b]	Approx. potential energy distribution, %[c]	ν_{Calc}, cm.$^{-1}$	ν_{Obs}, cm.$^{-1}$[a,d]	Approx. potential energy distribution, %[c]
Polypropylene-1,1-d_2[i]	2962	2961(vs)	r^-(100)	2962	2949(vs)	r^-(100)
	2962		r^-(100)	2962		r^-(100)
	2905		s(98)	2905	2904(s)	s(98)
	2882	2873(m)	r^+(98)	2882	2868(s)	r^+(98)
	2192	2169(w)	d^-(97)	2192	2171(s)	d^-(97)
	2088	2085(s)	d^+(97)	2091	2091(m)	d^+(97)
	1463	1452(s)	α(88)	1463	1461(s)	α(89)
	1461		α(90)	1462		α(90)
	1372		U(99)	1372	1377(s)	U(99)
	1344		ζ(56), S(42)	1339	1324(m)	ζ(65), S(18)
	1317	1327(m)	ζ(70)	1307	1303(w)	ζ(70), S(19)
	1194	1184(s)	ζ33, S(33), W(16)	1180	1170(s)	S(32), W(21), ζ(18)
	1125	1134(m)	β(34), R(16), ζ(14), ω(14)	1136		S(25), β(21), R(19), ζ(13)
	1081	1058(vs)	β(25), S(15), R(14)	1108	1110(m)	β(25), S(16), ω(14)
	1066	1060(vs)	δ(56), S(15)	1058	1050(s)	δ(76), W(20)
	1034	1013(s)	δ(25), R(22), β(19)	1029	1018(m)	β(25), R(24), W(20), S(15)
	887	894(m)	β(35), T(32), W(25)	902	896(m)	β(35), S(28)
	854	868(s)	β(34), W(29), S(21)	860		β(40), S(18)
	775	764(w)	T(26), S(22), R(20)	800	811(w)	T(45), W(16), P(13)
	700	691(m)	P(54), W(11), ω(8)	704	715(m)	P(31), W(17), S(16)
	427		ω(75), P(14)	486		ω(62)
	370		ω(57), ζ(18)	379		ω(56), ζ(26)
	241		ω(61), τ(16)	293		ω(70)
	195		τ(86)	197		τ(95)
	134		ω(49), τ(31)	140		ω(77), τ(19)
				61		τ(88)

Polypropylene-2-d_1	2962	2959(vs)	r^-(100)	2962		r^-(100)
	2962		r^-(98)	2961	2950(vs)	r^-(100)
	2928		d^-(99)	2928	2925(m)	d^-(99)
	2882	2886(s)[b]	r^+(98)	2882	2882(s)	r^+(98)
	2855	2868(w)	d^-(99)	2856	2867(m)	d^+(99)
	2158	2154(w)	s(96)	2156	2162(m)	s(96)
	1464		α(82)	1462	1459(s)	α(87)
	1460		α(87)	1461		
	1451	1451(s)	δ(79)	1452		δ(72)
	1375	1378(m)	U(78)	1374	1378(s)	U(84)
	1346	1342(m)	W(44), S(33)	1339	1334(s)	W(51), S(24), T(14)
	1267	1291(s)	T(29), W(21), S(18)	1287	1273(w)	T(41), S(19)
	1257		T(37), S(20), ζ(12), R(12)	1216		R(20), S(19), ζ(18), β(13)
	1155	1145(m)	β(30), S(17), W(15), ζ(15)	1161	1179(w)	β(23), S(22), T(21), ω(11)
	1057	1060(w)	β(37), P(13), ζ(11)	1082	1091(w)	β(32), R(15), P(10), ζ(9)
	981	981(s)	R(42), ζ(23), β(19)	1002	1005(w)	β(21), ζ(17), S(16), P(13)
	963	969(s)	β(39), S(30)	943	949(w)	β(43), S(36)
	901	881(w)	S(35), ζ(33), ω(19)	896		ζ(42), S(25), R(15)
	783	790(m)	ζ(48), ρ(26), R(16), S(13)	809	821(m)	ζ(42), R(21), β(18), S(17)
	756	754(m)	P(45), ζ(53)	777	791(m)	ζ(47), P(27)
	446		ω(80)	492		ω(60), ζ(11)
	387		ω(63), ζ(16)	422		ω(55), ζ(29)
	264		ω(58), τ(15), ζ(13)	308		ω(74)
	195		τ(88)	198		τ(94)
	138		ω(52), τ(28)	145		ω(76)
				62		τ(87)

(continued)

TABLE V (*continued*)

Polymer	*A* Block			*E* Block		
	$\nu_{Calc.}$, cm.$^{-1}$	$\nu_{Obs.}$, cm.$^{-1}$[a,b]	Approx. potential energy distribution, %[c]	$\nu_{Calc.}$, cm.$^{-1}$	$\nu_{Obs.}$, cm.$^{-1}$[a,d]	Approx. potential energy distribution, %[c]
Polypropylene-d_6	2214		r^-(95)	2215		r^-(88)
	2214		r^-(97)	2213		r^-(98)
	2190		d^-(95)	2194		d^-(80)
	2156		s(90)	2148		s(84)
	2086		d^+(96)	2090		d^+(96)
	2076		r^+(94)	2076		r^+(94)
	1291		S(88)	1256		S(57), R(23), W(21), ζ(16)
	1190		R(52), ζ(26)	1199		S(45), ζ(21), R(21), ω(18)
	1062		δ(45), U(30)	1072		U(46), δ(20), W(18)
	1058		U(44), α(22), δ(21)	1060		δ(41), U(20), W(14)
	1050		α(61), U(23)	1050		α(70), U(12)
	1049		α(80)	1049		α(85)
	1030		T(28), U(20), S(15), ω(13)	1038		U(20), β(10), α(9), δ(9)

981	$\zeta(30)$, $W(25)$, $\beta(14)$, $T(13)$	997	$S(18)$, $\beta(14)$, $W(12)$
924	$\zeta(30)$, $\beta(14)$, $\omega(10)$, $W(9)$	924	$\zeta(43)$, $S(11)$
886	$\zeta(39)$, $R(16)$, $S(11)$	889	$\zeta(35)$, $\beta(10)$, $S(10)$
774	$T(44)$, $W(15)$, $S(11)$	790	$T(48)$, $\zeta(15)$, $R(12)$, $W(10)$
750	$\beta(53)$, $W(20)$, $S(13)$	746	$\beta(50)$, $S(17)$, $W(11)$
682	$\beta(47)$, $\zeta(23)$	695	$\beta(43)$, $\zeta(19)$, $S(15)$
649	$P(54)$, $\zeta(27)$, $\beta(12)$	661	$P(32)$, $\beta(25)$, $\zeta(22)$
392	$\omega(70)$	449	$\omega(57)$, $S(9)$, $\zeta(8)$
334	$\omega(56)$, $\zeta(18)$, $\beta(12)$	353	$\omega(53)$, $\zeta(26)$
227	$\omega(56)$, $\zeta(11)$, $\tau(10)$	266	$\omega(69)$
143	$\tau(78)$	145	$\tau(75)$, $\omega(21)$
120	$\tau(44)$, $\omega(40)$	125	$\omega(58)$, $\tau(38)$
		55	$\tau(87)$

[a] Intensities: s, m, w, v, and sh mean strong, medium, weak, very, and shoulder.

[b] All bands which have been measured have a polarization direction parallel to the helix axis. Bands not measured are indicated.

[c] Potential energy distributions are given in per cent contribution to λ by the diagonal force constants for the following group coordinates: r, CH_3 stretch; d, CH_2 stretch; s, CH stretch, α, antisymmetric CH_3 bend; δ, CH_2 bend; U, symmetric CH_3 bend; W, CH_2 wag; T, CH_2 twist; P, CH_2 rock; ζ, CH bend; β, CH_3 rock; S, C—C chain stretching; R, C—CH_3 stretching; ω, C—C—C bend; and τ, C—C torsion.

[d] All bands which have been measured have a polarization direction perpendicular to the helix axis. Bands not measured are indicated.

[e] Unless otherwise indicated frequencies are from data of McDonald and Ward.[14]

[f] Data from Miyazawa et al.[13]

[g] Frequencies from Tobin.[16]

[h] Polarization not measured.

[i] Frequencies Peraldo and Farina.[15]

Our calculated frequencies for the crystalline isotactic forms of polypropylene, polypropylene-3,3,3-d_3, polypropylene-1,1-d_2, and polypropylene-2-d_1 are given in Table V. Observed frequencies for polypropylene are from the work of McDonald and Ward,[14] except for the low frequency modes of polypropylene which were reported by Miyazawa.[13] Frequencies for polypropylene-1,1-d_2, polypropylene-3,3,3-d_3, and polypropylene-2-d_1 are from Peraldo and Farina.[15] There is an excellent correspondence between the observed and calculated frequencies, with the polarization data on the observed frequencies matching the predicted polarization in all cases.

Vibrational assignments for isotactic polypropylene have been made by Tobin,[16] Krimm,[17] Liang and Pearson,[18] and McDonald and Ward.[14] An examination of our normal coordinates shows considerable mixing of the various CH_3, CH_2, and CH bending motions, as hinted at by Liang and Pearson. It is convenient to describe the normal modes of vibration in terms of group coordinates which can be loosely described as follows: (1) α, an antisymmetric CH_3 bend; (2) δ, a CH_2 bend; (3) U, the symmetric CH_3 bend or umbrella; (4) W, a CH_2 wag; (5) T, a CH_2 twist; (6) P, a CH_2 rock; (7) $\zeta^{\perp}$, a CH bend perpendicular to the H—C—CH_3 plane; (8) $\zeta^{=}$, a CH bend parallel to the H—C—CH_3 plane; (9) $\beta^{\perp}$, a CH_3 rock perpendicular to the H—C—CH_3 plane; (10) $\beta^{=}$, a CH_3 rock parallel to the H—C—CH_3 plane; (11) R, C—CH_3 stretching; (12) S, chain C—C stretching, and (13) ω, C—C—C bending. The normal coordinates of the A block of isotactic polypropylene and isotactic propylene-1,1-d_2 are presented in Figure 15. The lengths of the arrows are proportional to the elements of the $\boldsymbol{L}$ matrix. An examination of these modes indicates that in many cases it is not possible to assign a frequency to a single motion and in some cases not even to a single group (e.g., CH_3, CH_2, CH). Consider for example the CH_2 wagging frequency of polypropylene. The largest contribution to the normal vibration calculated at 1383 cm.$^{-1}$ is the CH_2 wagging but it is coupled strongly with the symmetric CH_3 bend, the CH bend, the CH_2 twist, and the CC stretch. In terms of the potential energy distribution the mode is described as follows, 27% CH_2 wag, 14% CH_2 twist, 20% CH_3 symmetric bend, 25% CH bend, and 26% C—C stretch. Now if we ask for the corresponding mode in polypropylene-1,1-d_2 we are faced with a difficult choice since the form of the normal modes is completely different in the deuterated molecule. The modes with significant amounts of CD_2 wag have the following potential energy distributions: 1197 cm.$^{-1}$ (16% CD_2 wag, 33% CH bend, 33% CC stretch and 4% C—CH_3 stretch); 887 cm.$^{-1}$ (25% CD_2 wag, 32% CD_2 twist, 9% CH bend, 35% CH_3 rock, and 6% CC stretch); 855 cm.$^{-1}$ (29% CD_2 wag, 4% CD_2 twist, 7% CH bend, 34% CH_3 rock, and 21% CC stretch).

None of these modes bear much relation to the so-called "CH_2 wag" in polypropylene; indeed, it is even difficult to decide which one to call CD_2 wag. The same difficulty arises with other modes. The only good correlation between the two sets of vibrations is between 1372 and 1370 cm.$^{-1}$, which are both predominantly CH_3 symmetric bending vibrations.

The disappearance of a band on the deuteration of a selected group indicates that the hydrogen motions of the group were involved in the vibration but does not indicate the extent or type of motion involved. We must conclude therefore the deuteration studies are of limited use in classifying the vibrational modes into CH, CH_2, or CH_3 motions. We would suggest that a careful study of the assignments and the determination of a good force field for a series of smaller related molecules followed by a normal coordinate calculation on the polymer is a more fruitful method of characterizing the vibrations of the polymer.

The force constants give in Table III were also used to calculate the spectra of two possible forms of syndiotactic polypropylene. Natta et al.[19] proposed a helical structure containing 4 monomers per translational repeat units, with a chain configuration which can be described as *trans-trans-gauche-gauche-trans-trans-gauche'* (ttgg'ttg'g'). The secular equation for the translational repeat unit contains 120 internal coordinates, and can be factored under the point group D_2, into matrices of order 32 (A, Raman), 28 (B_1, Raman, infrared), 30 (B_2, Raman, infrared), and 30 (B_3, Raman, infrared). There are 26 nonzero frequencies in each block.

A second structure for the syndiotactic polymer is possible. In this structure the translational repeat unit contains two monomers, and the chain configuration is tttt. This structure can be considered to be a substituted polyethylene. In this case the secular equation for the translational repeat unit contains 60 internal coordinates and can be factored under the point group C_{2v}, into equations of order 19 (A_1, Raman, infrared), 13 (A_2, Raman), 11 (B_1, Raman, infrared), and 17 (B_2, Raman, infrared).

A comparison of the calculated infrared active frequencies of the two proposed structures indicates that it should be possible to decide between them from the infrared spectrum of crystalline syndiotactic polypropylene between 1300 cm.$^{-1}$. To this date, however, the spectrum has not been reported in the literature.

Summary

With only slight changes, the well known methods of calculating vibrational frequencies and normal coordinates of molecules may be applied also to polymers. In the case of polymers however, *ab initio* assignments are usually very risky since the spectra of these systems tend to be rather complex. It is reasonable therefore to determine a force field for a given polymer from an analysis of the vibrations of a series of simple molecules closely related to it. The resulting force field derived from and common to these molecules, may then be used to calculate the spectrum of the polymers with the expectation that the error between the calculated and observed frequencies will be about the same as that found for the vibrations of the molecules used to determine the force field. We have calculated the vibrational frequencies of polyethylene and isotactic polypropylene, using valence force field derived from *n*-paraffins (270 frequencies) and branched paraffins (308 frequencies). The error between the observed

and calculated frequencies is less than 1% for both the molecules and the polymers, including four deuterated isotactic polypropylenes. In the case of polypropylene many of the modes are found to be a complex mixture of internal coordinates. Upond euteration the form of these vibrations is often changed so drastically that it is impossible to identify the analogous band in the spectrum of the deuterated sample. This is a fact which should once again remind us that great caution must be exercised in drawing conclusions about the character of normal modes from the spectrum of isotopically substituted analogues. Finally, the frequencies of syndiotactic polypropylene were calculated for two possible forms of this polymer. The calculated frequencies of the two forms are quite different and should, when the observed spectrum becomes available, help to identify the correct structure.

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Discussion

T. Miyazawa (*Osaka University, Osaka, Japan*): I have two rather small questions for Dr. Schachtschneider. In your calculations you have used a *trans* interaction term in the potential energy function for the C—C—C angles. Do you also introduce a *gauche* interaction for a pair of bond angles?

J. H. Schachtschneider: We did include a *gauche* interaction but it does not really matter whether you put it in or leave it out. That term is one of those that turned out to have a dispersion which is about twice the value of the constant that you calculate. That term is unimportant for reproducing the frequencies.

T. Miyazawa: How many potential constant did you actually use for treating isotactic polypropylene?

J. H. Schachtschneider: We have used 28 force constants out of the 35 which have been calculated for the branched paraffins. I would like to emphasize again that we made no adjustment of the force constants in calculating the frequencies of isotactic and syndiotactic polypropylene.

P. Corradini (*Istituto Chimico Napoli, Italy*): We have obtained a very good x-ray spectrum of syndiotactic polypropylene and from that spectrum the identity period has been well established. Furthermore the x-ray spectrum has about 20 or 30 reflections in the different layer lines. We have done some calculations up to the third layer line. I think that the helical structure with twofold axes perpendicular to the chain axis is now completely established for the crystalline polymer. I wonder what the infrared spectrum of that substance looks like.

J. H. Schachtschneider: As for the planar structure of syndiotactic polypropylene the only reference I can refer to is a lecture given by Dr. Flory at the University of California. Dr. Flory has said that some Russian scientists had proposed that the planar structure was certainly a possible one. I have not been able to obtain any definite reference or information on this. Anyhow I think the calculation is interesting in that it does point out that there is quite a difference in the spectra, depending on the structure.

P. Corradini: Some Russian scientists have theoretically predicted that the chain of polypropylene could well exist in the TT conformation. If you assume that the energies of TT and GG conformations are about the same, certainly in solution TT conformation should be more probable than the GG conformation. In fact if the energies of TT and GG forms are taken to be the same and if we do not allow the GG form to be followed by another GG form, statistical thermodynamics show that there may exist about three TT sequences for one GG sequence for syndiotactic polypropylene in unperturbed solution. These are the reasons which suggest that the TT sequences may be present to some extent also in the crystal state of syndiotactic polypropylene.

S. Krimm (*University of Michigan, Ann Arbor, Michigan, U.S.A.*): Do you have any idea what stabilizes the TT and GG forms in the crystal?

P. Corradini: One may try to understand this problem by looking at the interaction energies between CH_3—CH_3 and CH_3—CH_2 groups. The number of contacts between CH_3 and CH_3 groups in the trans form of the syndiotactic polypropylene is the same as the number of CH_3—CH_2 contacts in the helical chain. The shortest distance between two CH_3 groups in trans syndiotactic polypropylene is about 3.68 A., a little shorter than the generally observed for a CH_3—CH_3 distance in organic molecules in the crystalline state. Bunn has suggested, and I agree with him, that the interaction energy between CH_3 and CH_2 groups at a distance of 3.68 A., which occurs in the helical compounds, may be lower because of a lower hindrance. In such a case the GG conformation may be more stabilized in the crystal because it gives rise to a greater number of CH_3—CH_2 contacts.

S. Krimm: Is it possible that interchain interactions stabilize the GG form?

P. Corradini: Of course, if the energies of the two possible isolated chains are the same, interchain forces which arise in the crystal may stabilize one form more than the other.

T. Shimanouchi (*Tokyo University, Tokyo, Japan*): The factors which determine the stability of the various conformers as well as the height of potential energy barrier are one of the most puzzling problems in the field of physical chemistry. Dr. E. Bright Wilson at Harward has done a great deal of work in this direction. If we want to know the energy difference between two possible structures one should try at least to have some information about the forces between two hydrogen atoms.

As to the problem of the force field in normal coordinate calculations I should like to add some comment. In our laboratory at the beginning we have used the pure Urey-Bradley force field for the purpose of assigning the vibrational bands. For that purpose UBFF works very well. But if we want to do more accurate normal coordinate analysis

the simple UBFF is not enough. In our group we start from UBFF and we modify it in the direction of a valence force field. Dr. Schachtschneider has used a valence force field and I think it is very important to compare his results with those obtained from a UBFF.

J. H. Schachtschneider: I think that one could have more confidence in our calculations if from two different starting points we could converge to very nearly the same sets of normal coordinates instead of potential energy distributions.

T. Miyazawa: In the past years the Valence Force Field (VFF) and the central force field (CFF) were mainly used in normal coordinate calculations. Central force field takes into account the interactions between every pair of atoms. Valence force field is closer to our chemical feeling. About ten years ago Dr. Linnett in England had proposed a new force field which has been called orbital force field. More recently a great deal of work has been done with the Urey-Bradley force field (UBFF). I think that UBFF can actually be derived from a combination of CFF and VFF. More recently UBFF has been modified by Dr. Shimanouchi, Dr. Crawford, and Dr. Overend with the introduction of several other terms like the *trans* and *gauche* coupling etc. in order to give better frequencies. I think all these new terms correspond quite closely to the constants of the orbital force field. In conclusion by using a modified Urey-Bradley force field we are now in a better position.

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Infrared Spectra of a Few Synthetic Polyribonucleotides

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INTRODUCTION

Infrared spectra of nucleic acids are expected to be greatly useful in elucidating a part of their structure, if reliable assignments are established to the absorption bands observed. Synthetic polyribonucleotides[1] have exactly the same chemical structure as the natural ribonucleic acids (RNA's), except that their base compositions and base sequences are different. The base compositions and sequences of the synthetic polynucleotides can be controlled to some extent. Therefore, investigations of the vibrational spectra of these polymers would produce a mass of information having a direct bearing on the vibrational spectra of natural ribonucleic acids. In this paper, infrared spectra of four homopolymers, polyribocytidylic acid (poly-C), polyriboadenylic acid (poly-A), polyribouridylic acid (poly-U), and polyriboinosinic acid (poly-I), are subjected to the discussion. Infrared spectra of these homopolymers are certainly much simpler and more easily interpreted than the spectra of natural complicated copolymers. Nevertheless, the band assignment is in general still a quite difficult problem because the structural units are very large and complex. In approaching a solution of this problem, the six following methods may be used.

(*1*) Comparison of the spectra of these homopolymers with one another. Most vibrations corresponding to the absorption bands in the 4000–400 cm.$^{-1}$ region of polynucleotides would be localized either in the base residues or in the ribose-phosphate main chain. Absorptions due to the main chain vibrations would appear in every homopolymer, while absorptions due to base residue vibrations would be characteristic of a certain homopolymer.

(*2*) Examination of the effects of humidity. Some polynucleotides show in some conditions a high crystallinity. Such a crystallinity is in general sensitive to the humidity of the surrounding air. In a dry atmosphere the crystallinity is usually much lower than in a humid atmosphere. Thus, by controlling the humidity of the surrounding atmosphere, we may observe a different spectra in the same sample with higher and lower crystallinities.

(*3*) Examination of the anisotropy of the absorptions. For some polynucleotides, under certain conditions, well oriented films can be obtained.

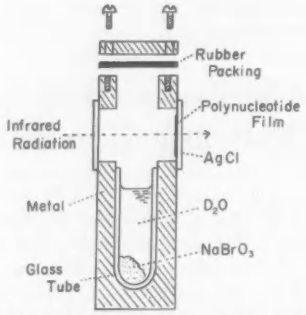

Fig. 1. Infrared absorption cell in which polynucleotide film can be deuterated.

Observation of the infrared dichroism of such films is very helpful in understanding the nature of the absorption bands, as it is in any other high polymer studies.

(*4*) Examination of the effects of deuteration. Polynucleotides, unlike other polymers, can be deuterated almost completely through vapor phase exchange. When the sample film is placed in a sealed cell, as shown in Figure 1, and a D_2O solution (for example, a saturated solution of sodium bromate in D_2O) is placed on the bottom of this cell, virtually all the hydrogen atoms (except those of the CH bonds) both in the crystalline part and in a less crystalline part are replaced by deuterium atoms. In this way, a spectral comparison can be made of deuterated and undeuterated films of exactly equal thickness.

(*5*) Comparison of the spectra of films cast from solutions of different pH's. By this comparison, any spectral change due to the protonation or deprotonation of the base residue may be observed.

(*6*) Comparison of the spectrum in question with the spectrum of a simple molecule which is considered to form a part of the polynucleotide chain and of whose absorption bands reliable assignments have been made.

By means of these methods, the natures of several absorption bands of the polynucleotides have now been clarified.

1750–1500 CM.$^{-1}$ REGION

The absorption bands in the 1750–1500 cm.$^{-1}$ region can be assigned for the most part to the in-plane vibrations of the base residues with pyrimidine and purine rings. No significant contribution by the phosphate units or by the sugar unit can be expected in this region.

Bands due to Cytosine Residue

Polycytidylic acid (poly-C) film cast from a solution of pH 5.5 shows five bands at 1730, 1655, 1615, 1530, and 1500 cm.$^{-1}$ in this spectral region (Fig. 2). On deuteration these are shifted respectively to 1700, 1650, 1610, 1525, and 1503 cm.$^{-1}$.

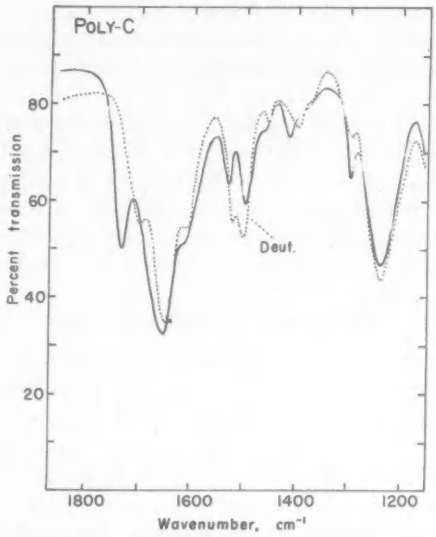

Fig. 2. Infrared absorption spectra of poly-C film cast at pH 5.5 and placed in air at 75% R.H.: (——) undeuterated; (. . .) deuterated.

Of these five bands, the 1730 cm.$^{-1}$ (1700 cm.$^{-1}$ on deuteration) band is absent in the film cast from a solution of pH 7.3. This band corresponds to the 1725 cm.$^{-1}$ (1709 cm.$^{-1}$ on deuteration) band of cytidine,[2] and is assigned to the C=O stretching vibration of the cytosine residue, protonated at position N_1. Thus, it is seen that, in poly-C, appreciable protonation of the base residue takes place at pH 5.5. In both of protonated poly-C and protonated cytidine, the observed deuteration effect of the 1730 cm.$^{-1}$ band may be taken as indicating that, in the protonated cytosine residue, the contribution of N^+—H in-plane bending mode at N_1 to the C=O stretching vibration is appreciable. This contribution is considered to be greater in protonated poly-C than in protonated cytidine, because the deuteration effect is observed to be greater in the 1730 cm.$^{-1}$ band in the former than that in the 1725 cm.$^{-1}$ band in the latter.

Recently, Akinrimisi, Sander, and Ts'o[3] suggested that poly-C in acidic solution assumes a secondary structure where the protonated cytosine residue makes a pair with the unprotonated cytosine residue through the N_1^+—H. . . . . N_1 hydrogen bond. Based upon their suggestion, an examination of the effect of secondary structure formation on the 1730 cm.$^{-1}$ band is now going to be made.

The strong 1650 cm.$^{-1}$ band of deuterated poly-C is considered to correspond to a superposition of the strong 1652 cm.$^{-1}$ band of neutral deuterated cytidine and the strong 1658 cm.$^{-1}$ band of deuteronated cytidine.[2] The weak 1610 cm.$^{-1}$ band of deuterated poly-C may be correlated with the weak 1615 cm.$^{-1}$ band of neutral deuterated cytidine.[2] On the other hand,

the counterparts of the 1655 (strong) and 1615 (weak) cm.$^{-1}$ bands of undeuterated poly-C film are found in cytidine at somewhat different frequencies (at 1680, 1670, 1647, and 1603 cm.$^{-1}$) with greatly different relative intensities.

The two bands at 1530 and 1500 cm.$^{-1}$ of undeuterated poly-C and two stronger bands at 1525 and 1503 cm.$^{-1}$ of deuterated poly-C seem to be characteristic bands of neutral cytosine residue. In poly-C and cytidine, the spectral features of these bands are alike to each other. No strong absorptions appear in this spectral region in poly-A, poly-U, and poly-I. These may possibly be useful for a certain analytical purpose.

Bands due to Adenine Residue

It is known that poly-A film cast from acidic solution shows a high degree of crystallinity. Morgan and Blout[4] made an observation of infrared dichroism of such a film. We have made similar observation with a sample of a slightly higher crystallinity, under controlled humidities, and in wider spectral region (down to 400 cm.$^{-1}$). The results are given in Figure 3.

In the spectral region, now in question, deuterated poly-A (cast from a solution of pH 5) shows two strong bands at 1660 and 1620 cm.$^{-1}$. As may be clearly seen in Figure 4, the former is due to the protonated and

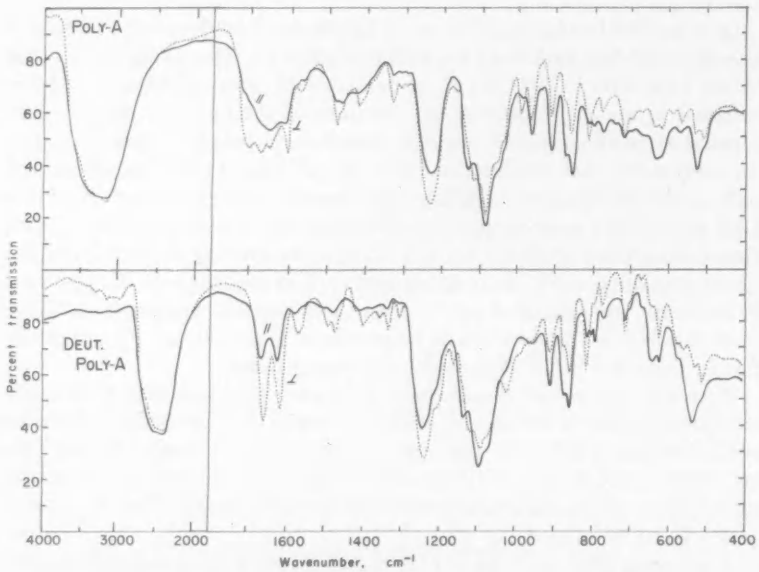

Fig. 3. Infrared absorption spectra of oriented poly-A film cast from an aqueous solution of pH 5 (top) in H_2O vapor, at 92% R.H., and (bottom) in D_2O vapor, at 92% R.H.: (——) electric vector of the incident radiation parallel to the fiber axis, (. . .) electric vector of the incident radiation perpendicular to the fiber axis.

the latter to the neutral adenine residue. Both of these bands are to be assigned to some ring vibrations in which the C=N stretching motions predominate. From the strong perpendicular dichroism observed (Fig. 3),

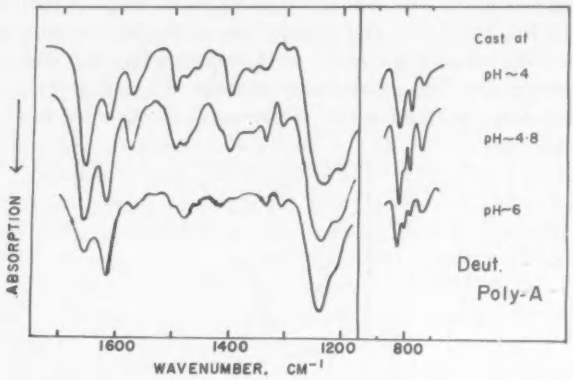

Fig. 4. Infrared absorption spectra of poly-A films cast from aqueous solutions of pH 4, 4.8, and 6; observed in D_2O vapor at 92% R.H.

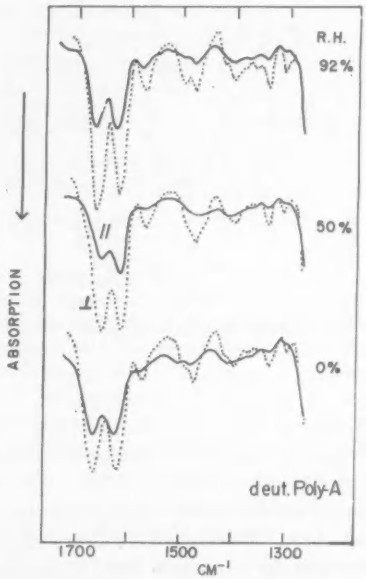

Fig. 5. Observed absorption spectra of oriented and deuterated poly-A film (cast at pH 5) placed in the air of different humidities: (——) electric vector of the incident radiation parallel to the fiber axis; (. . .) electric vector of the incident radiation perpendicular to the fiber axis.

it may be concluded that both protonated and neutral adenine residues are predominantly perpendicular to the orientation axis. The dichroic ratio ($\perp/\parallel$) is always slightly higher for the 1660 cm.$^{-1}$ band than for the 1620 cm.$^{-1}$ band. In an atmosphere (air) of 92% R.H., it is estimated that the transition moment of the former makes an angle of 66° (or a little larger) with the fiber axis, and that of the latter 64° (or a little larger). On reducing the relative humidity of the surrounding air, the dichroism certainly goes down (Fig. 5), probably because of a partial loss of crystallinity. However, the effect is not as marked as is observed in the case of

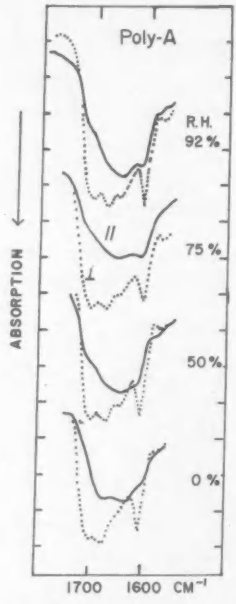

Fig. 6. Infrared absorption spectra of oriented and undeuterated poly-A film (cast at pH 5) placed in air of different humidities: (——) electric vector of the incident radiation parallel to the orientation axis; (. . .) electric vector of the incident radiation perpendicular to the orientation axis.

DNA.[5] Even at 0% R.H., fairly high dichroism is observed (see Fig. 5). The role of the water molecules seems to be less important for the secondary structure formation in acid poly-A than in DNA. Two bands of deuterated poly-A with medium intensities at 1570 and 1500 cm.$^{-1}$ are attributed to acidic adenine residue (see Fig. 4). These appear only when the residue is deuterated, and are therefore assigned to some in-plane vibrations where more or less N_1D^+ and/or ND_2 in-plane deformations take place. The perpendicular dichroism (Fig. 3) observed of these two bands is consistent with the arrangement of the adenine residue perpendicular to the orientation axis.

Undeuterated film of poly-A cast at pH 5 shows a strong band at 1720 cm.$^{-1}$ (Figs. 3 and 6) in air at 92% R.H. This band is considered to correspond to the 1693 cm.$^{-1}$ band of protonated adenosine[2] and to be assigned to a coupled vibration of the NH_2 bending and C=N and C=C stretching motions. The in-plane bending mode of the N^+—H group at N_1 would also make a contribution to the vibration. The fact that this frequency is much higher in polyadenylic acid than that in protonated adenosine may be explained by taking the double-helix structure[6] into account. In this structure, each NH_2 group in one of the two helices is considered to be involved in two strong hydrogen bondings, N—H. . . . O and N—H . . . . N, respectively with the PO_2^- group and with the position-7 nitrogen of a nucleotide residue in the other helix. The position-1 N^+—H may also be involved in strong hydrogen bonding, as for example, the hydrogen bond to a water molecule, strongly bound to the PO_2^- group. The NH_2 and N^+H groups in the protonated adenosine crystal would not be involved in such strong hydrogen bonds, as there is no PO_2^- group. On drying the film, the 1720 cm.$^{-1}$ band is shifted to 1700 cm.$^{-1}$ (see Fig. 5). This is probably due to breakdown of some of the hydrogen bonds mentioned above.

It has been shown[7-9] that the 1708 cm.$^{-1}$ band of deoxyribonucleic acid (DNA) is a characteristic band of its secondary structure. Drying, heating, and some other treatments of DNA cause the disappearance of this band. The behavior of the 1720 cm.$^{-1}$ band of acid poly-A just mentioned appears to be somewhat similar to that of the 1708 cm.$^{-1}$ band of DNA.

Bands due to Other Base Residues

Poly-U film cast at pH 6.6 and poly-I film cast at pH 6.2 give a strong, broad band at about 1680 cm.$^{-1}$. No marked effects due to deuteration and the humidity of the surrounding air have been observed.

1500–1300 CM.$^{-1}$ REGION

2′-OH In-Plane Deformation Bands

For polyribonucleotides, absorption due to the OH in-plane deformation at the position 2′ of the ribose residue is expected to appear in this region. This OH group is that of a secondary alcohol, and hence reference to the spectrum of isopropyl alcohol[10] may be helpful. Undeuterated isopropyl alcohol, in the liquid state, shows strong bands at 1412 and 1311 cm.$^{-1}$ (Fig. 7), both of which are assigned to vibrations where OH and CH in-plane bendings are coupled with each other. On deuteration, both of these bands disappear, and a new weak band appears at 1342 cm.$^{-1}$ which is assigned to almost pure CH in-plane bending. (This band is superposed upon another CH bending band at the same frequency.) Deuterated acid poly-A shows a weak band at 1360 cm.$^{-1}$ which is absent in undeuterated acid poly-A (see Fig. 3). This may correspond to the 1342 cm.$^{-1}$ (CH

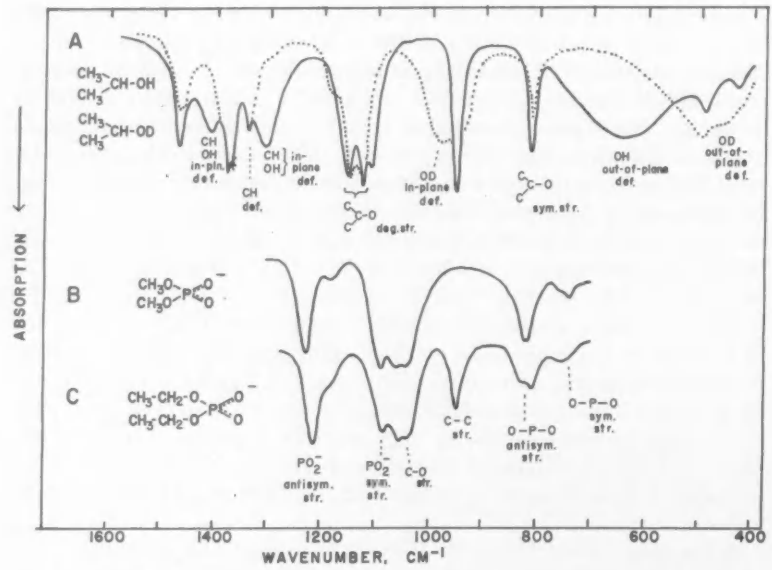

Fig. 7. Infrared absorption spectra of a few compounds related to polyribonucleotides: (*A*) isopropyl alcohol (——) undeuterated and (. . .) *O*-deuterated in the liquid states;[10] (*B*) dimethyl phosphate in aqueous solution;[9] (*C*) Diethylphosphate in aqueous solution.[9]

deformation) of deuterated isopropyl alcohol. In undeuterated poly-A, there are weak bands at 1320 and 1420 cm.$^{-1}$; both of them are absent in deuterated poly-A. These two (both with perpendicular dichroism) are suspected to be due to the coupled vibrations of 2′-OH and 2′-CH deformation modes.

1300–1000 CM.$^{-1}$ REGION

PO_2^- Stretching Bands

In this spectral region, two strong absorption bands are expected to appear due to the $(O\cdots P\cdots O)^-$ group: one due to PO_2^- antisymmetric stretching and the other due to PO_2^- symmetric stretching.[11] There would be no objection to assigning the isolated, strong band at 1230 cm.$^{-1}$ to the PO_2^- antisymmetric stretching vibration.[5,11] The PO_2^- symmetric stretching vibration is most probably assigned to the strong band at 1090 cm.$^{-1}$ Barium dimethylphosphate shows[9] a strong and polarized Raman line at 1085 cm.$^{-1}$ in its aqueous solution, and barium diethylphosphate shows[9] a similar, strong, and polarized Raman line at 1088 cm.$^{-1}$. These are assigned to the PO_2^- symmetric stretching vibration. The corresponding infrared bands of these phosphates are as strong as the 1220 cm.$^{-1}$ band

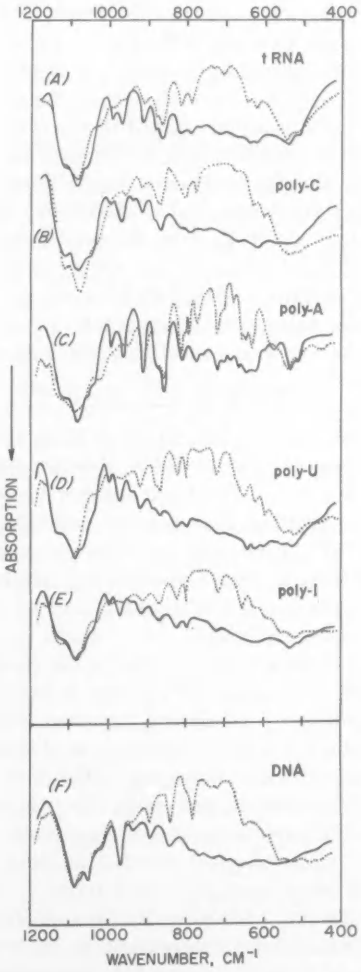

Fig. 8. Infrared absorptions in the 1100–400 cm.$^{-1}$ region for (——) undeuterated and (. . .) deuterated materials: (*A*) yeast transfer RNA (bulk) film cast from neutral (potassium salt) aqueous solution, at 92% R.H.; (*B*) poly-C film cast from aqueous solution, pH 4.4, at 92% R.H.; (*C*) poly-A film cast from aqueous solution, pH 4.5, at 75% R.H.; (*D*) poly-U film cast from aqueous solution, pH 6.6, at 92% R.H.; (*E*) poly-I film cast from aqueous solution of pH 6.2, at 92% R.H.; (*F*) calf thymus DNA film cast from neutral aqueous solution, at 92% R.H.

(Fig. 7), although on going from aqueous solutions to the solid states the intensities are slightly lowered. For poly-C, poly-A, poly-U, poly-I, RNA, and DNA, a strong absorption peak is observed at about 1090 cm.$^{-1}$ (see Fig. 8).

The PO_2^- antisymmetric stretching vibration would have its transition moment nearly along the direction of the O. . . . .O line of the PO_2^- group, and the PO_2 symmetric stretching vibration is nearly along the bisector of the angle OPO. Therefore, the dichroism of these two bands observed with poly-A film (Fig. 3) must be related to the orientation of the PO_2^- group in it. As may be seen in Figure 3, the 1230 cm.$^{-1}$ band shows perpendicular dichroism and the 1090 cm.$^{-1}$ band parallel dichroism. The dichroic ratios ($\parallel/\perp$) are determined to be 0.68 for the 1230 cm.$^{-1}$ band and 1.23, for the 1090 cm.$^{-1}$ band in the undeuterated and deuterated films at 92% R.H. Therefore, the O. . . . .O line of the PO_2^- group must be inclined about 60° or more, and the OPO bisector must be inclined about 52° or less to the orientation axis. In the poly-A model of Rich, Davies, Crick, and Watson,[6] these are, respectively, 68° and 41°.

The 1120 cm.$^{-1}$ Band

One of the marked spectral differences of RNA from that of DNA is found in the 1120 cm.$^{-1}$ region.[5] RNA shows a band at 1120 cm.$^{-1}$, while this is absent in DNA. This band appears not only in every natural ribonucleic acid examined but also in every synthetic polyribonucleotide examined (see Fig. 8). This band undergoes almost no effect on deuteration. Based on these facts and based on the frequency value, this band may be assigned to a stretching vibration of a skeletal structure around the 2′-OH group of the ribose residue.

In RNA, a strong absorption is expected to be caused by the $C_{2'}$-(OH) stretching vibration. Its intrinsic frequency is considered[12] to be about 1000 cm.$^{-1}$. In the normal vibrations, however, this stretching motion should couple with the C—C stretching motions of the nearby C—C bonds whose intrinsic frequencies are also about 1000 cm.$^{-1}$. The coupling may be somewhat similar to that in isobutane,[13] isopropyl alcohol,[10] and isopropylamine.[14] In the latter molecules, a degenerate or nearly degenerate stretching vibration takes place at about 1120 cm.$^{-1}$, and a symmetric stretching vibration takes place at about 810 cm.$^{-1}$ (for isopropyl alcohol see Fig. 7). The 1120 cm.$^{-1}$ band of polyribonucleotides, now in question, may therefore be considered to correspond to such a nearly degenerate stretching vibration. Corresponding to the frequency, 810 cm.$^{-1}$, of isobutane, isopropyl alcohol, and isopropylamine, a medium intensity band is observed at about 810 cm.$^{-1}$ in RNA and synthetic polyribonucleotides. This band is also unaffected by deuteration, and it is absent in DNA (see Fig. 8 and text below).

With the polarized radiation, the 1120 cm.$^{-1}$ band of poly-A is found to consist of two components (see Fig. 3). Thus, with the infrared radiation polarized parallel to the fiber axis an absorption peak is observed at 1135 cm.$^{-1}$, while with the radiation polarized perpendicular to the fiber axis, a shoulder is observed at 1116 cm.$^{-1}$. This fact shows that there are two vibrations in this frequency region, whose transition moments are directed nearly perpendicular to each other. This may be taken as an additional

support of the interpretation that the 1120 cm.$^{-1}$ band of RNA is due to a nearly degenerate C—O stretching vibration.

2′OD In-Plane Deformation Band

For deuterated alcohols, the intrinsic frequency of the COD in-plane deformation vibration is considered to be about 1000 cm.$^{-1}$. In the primary alcohols, this deformation mode may couple with the skeletal stretching modes which take place also in the vicinity of 1000 cm.$^{-1}$. In the secondary alcohols, on the other hand, the skeletal stretching frequencies do not occur in the vicinity of 1000 cm.$^{-1}$ (as mentioned above), and therefore an almost pure C—O—D in-plane deformation band is expected at about 1000 cm.$^{-1}$. In fact, *O*-deuterated isopropyl alcohol shows a medium intensity band at 983 cm.$^{-1}$ (see Fig. 7), which is certainly assignable to the COD in-plane deformation vibration.[10] Also, deuterated cellulose shows absorptions in the 1000–1030 cm.$^{-1}$ region which are absent in undeuterated cellulose.[15]

Deuterated RNA shows a weak and broad band at about 1020 cm.$^{-1}$ which is absent in undeuterated RNA (Fig. 8). A similar band appears also in deuterated poly-C, deuterated poly-A, deuterated poly-U, and deuterated poly-I, but not in their undeuterated forms (Fig. 8). In deuterated DNA no counterpart of this band is found around 1000 cm.$^{-1}$. Deuterated DNA does show a 1015 cm.$^{-1}$ band, but this is observed with almost the same intensity at almost the same frequency in undeuterated DNA (Fig. 8). Our preliminary experiment shows that this band is also absent in deuterated and *O*-methylated RNA (kindly donated by Professor F. Egami, Tokyo University). Thus, it is probable that the weak and broad 1020 cm.$^{-1}$ band of deuterated polyribonucleotides is due to the 2′OD in-plane deformation vibration.

In all of the spectra of natural and synthetic polyribonucleotides shown in Figure 8 a band near 1050 cm.$^{-1}$ disappears upon deuteration. Therefore, one might consider that the 1020 cm.$^{-1}$ band in the deuterated species arises from this band. At least in poly-A, however, this is not probable, because the dichroic properties of the 1050 cm.$^{-1}$ band of undeuterated poly-A is quite different from that of the 1020 cm.$^{-1}$ band of deuterated poly-A. In oriented fibers of deuterated poly-A obtained from an acidic solution, this band at 1022 cm.$^{-1}$ shows a marked perpendicular dichroism, while absorptions in the 1050 cm.$^{-1}$ region of the undeuterated poly-A film do not show such a marked anisotropy (Fig. 3).

1000–400 CM.$^{-1}$ REGION

NH_2 and ND_2 Wagging and OH and OD Out-of-Plane Deformation Bands

Adenine and cytosine residues have the amino group at position 6. Therefore, in their spectra, a fairly strong and broad band due to the NH_2

wagging vibration is expected to be observed somewhere in the 900–500 cm.$^{-1}$ region. Almost in the same spectral region, a broad band due to the ribose-2′-OH out-of-plane deformation vibration is also expected to occur in all natural and synthetic polyribonucleotides. Both of them should disappear upon deuteration.

As may be seen in Figure 3, there is a broad background absorption in the 900–600 cm.$^{-1}$ region, which shows parallel dichroism and which disappears on deuteration. The adenine residue is known to be oriented with its plane almost parallel to the orientation axis. Therefore, the transition moment of the NH_2 wagging band would be directed almost parallel to the orientation axis. Thus, a part of the above-mentioned 900–600 cm.$^{-1}$ band may be assigned to the NH_2 wagging in question, but a part of it may be due to the ribose-2′-OH out-of-plane deformation. The latter also may show possibly parallel dichroism. A superposition of the band due to the absorbed H_2O is also expected here, which, however, would not show any anisotropy.

ND_2 wagging band of deuterated poly-A is expected in a lower frequency region, 600–400 cm.$^{-1}$. In a relatively narrow region, 570–530 cm.$^{-1}$ fairly strong background absorption is observed which is much stronge, with the infrared radiation polarized parallel to the fiber axis (see Fig. 3)r This is not observed with undeuterated poly-A. Also in the 500–400 cm.$^{-1}$. region, a broad absorption band is observed with parallel dichroism. This is a little weaker than the background absorption in the 570–530 cm.$^{-1}$ region. For isopropyl alcohol the band due to the OD out-of-plane deformation vibration is observed at about 470 cm.$^{-1}$ (Fig. 7). Therefore, the broad 500–400 cm.$^{-1}$ band may tentatively be assigned to the out-of-plane deformation vibration of the ribose-2′-OD group, and the 570–530 cm.$^{-1}$ absorption to the position-6 ND_2 wagging vibration.

From the dichroism observed of the 1020 and 470 cm.$^{-1}$ bands of poly-A (Fig. 3), it is suggested that in the poly-A fiber the $C_{2'}$—$O_{2'}$—H is in the plane perpendicular to the fiber axis. In the structural model of this polymer presented by Rich et al.[6] the $C_{2'}$—$O_{2'}$ bond is directed perpendicular to the fiber axis, in agreement with the suggestion given here.

The 790 cm.$^{-1}$ Band of Poly-A

In deuterated poly-A, there is an interesting band at 790 cm.$^{-1}$. This band is very sharp and shows a strongly parallel dichroism (Fig. 3). It appears only in deuteronation (D^+) poly-A. Its intensity depends upon the degree of deuteration of the deuterated adenine residue (see Fig. 4). Therefore, the band in question of poly-A may be assigned to an out-of-plane vibration of the deuterated adenine residue, probably involving the N^+—D out-of-plane deformation mode at position 1.

Other Characteristic RNA Bands

Besides the bands mentioned above, there are a number of well-defined absorption bands in polyribonucleotides. Many of them appear in all the

synthetic polyribonucleotides and in all natural RNA's so far examined at almost the same frequencies with almost equal relative intensities. These are at 995 (m), 970 (m), 915 (s), 880 (m), 870 (s), 815 (s), 530 (s), and 510 (m) cm.$^{-1}$ (see Fig. 9). The first two of these (995 and 970 cm.$^{-1}$ bands) disappear on deuteration, and the other six remain almost unchanged. All of these bands may be attributed to ribose-phosphate main-chain vibrations.

The 815 cm.$^{-1}$ band may be assigned to the 2′ C—C(C)—O symmetric stretching vibration, as has been mentioned above. However, there is another possibility that it is due to the O—P—O single bond antisymmetric stretching vibration (see Fig. 7).

It is noteworthy that almost none of these bands appear in DNA. In DNA a quite different set of absorption bands is observed (see Fig. 8). This fact suggests that all the synthetic and natural polyribonucleotides have a common local conformation, which is quite different from that of DNA.

The infrared absorption spectra of synthetic polyribonucleotides presented in this paper were obtained in cooperation with Mrs. K. Matsuo, and Mr. H. Koike. Experimental details will be published elsewhere.

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CONTRIBUTED PAPERS

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Classification of Crystallinity Bands in the Infrared Spectra of Polymers

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INTRODUCTION

A substantial contribution to the knowledge of polymers has been made by infrared spectroscopy.[1,2] The qualitative and quantitative data obtained from the infrared spectra have been largely used in the study of the polymerization processes and for the elucidation of the structure of these very complex organic molecules. In order to obtain polymers showing superior chemical and mechanical properties, a great deal of work has been carried out by many polymer chemists on the synthesis of regular or stereoregular polymers possessing a high degree of crystallinity.[3] For these reasons infrared spectroscopists have been asked to find new methods for the determination of the degree of regularity and of the crystallinity content of a given sample. Many attempts have been made to find in the spectrum bands which may be characteristic of a given structure of the substance under study; this work may be traditionally defined as a search for crystallinity bands.

We feel that at the present stage of the research in this field it is necessary to reanalyze the meaning of the term "infrared crystallinity bands." The purpose of this paper is to report an analysis of the problem and an attempt of classification of such bands according to the structure and phases of the polymeric substances.

The interpretation of the infrared spectrum of a polyatomic molecule has been generally carried out from two different viewpoints. The first one is based on the rigorous determination of the vibrational levels of the molecule considered in first approximation as a system of coupled harmonic oscillators.[4] The fundamental transitions and their optical activity are determined by the quantum mechanical selection rules. The second method consists in the use of empirical correlations which associate some of the infrared bands with the presence of groups of vibrating atoms.[5] The study of the infrared spectra of polymers can be carried out with the same methods. Whereas the former can be applied when the polymer is

relatively simple, the latter can give some basic information when the polymer chain is so complex as to prevent the application of any theoretical treatment. However, because of the peculiar aspect of the dynamics of the polymer molecule we can obtain from the spectrum some other information useful for structural studies.

APPLICATION OF CHARACTERISTIC GROUP FREQUENCIES

We start our classification from the information one can obtain from the correlative study of the spectra of polymers. Correlations are mainly based on the following approximations: (*a*) some of the atomic groups in the polymer molecule vibrate independently of the remainder of the molecule and give rise to characteristic absorptions; (*b*) the mechanical coupling between the various vibrating groups within the molecule is either zero or small enough to be neglected; (*c*) frequency variations can be ascribed mainly to changes of the masses, to rearrangement of the electronic distribution within the vibrating group, and to the variations of the surrounding of the group.

On the basis of these approximations several empirical correlations have been found which enable one to recognize the chemical nature of an unknown polymer sample. As an example one can easily distinguish between the various polybutadienes (1,4-*cis*, 1,4-*trans*, and 1,2).[6] In the same way we can obtain useful information on the polymerization processes which take place during the reaction(head-to-tail inversion, branching, etc.).

A more careful analysis based on spectral correlations can give more useful information on the structure of the polymers. In fact, when dealing with the structure of the polymer molecules, one always has to deal with the possible presence of several rotational isomers[7] and of special steric configurations.[8] It has been empirically found that it is sometimes possible to associate some of the infrared bands with the occurrence of certain structures in the polymer molecule.

Conformational Bands

On the basis of the previous discussion we introduce our first definition: some of the bands observed in the infrared spectrum of a polymer substance may be called "conformational bands" if: (*1*) with the help of the existing spectral correlations (or with some new ones eventually found with the study of model compounds) they can be associated with well defined configurations of certain atomic groups existing in the chemical repeating unit, the transformation from one configuration to the other being obtained only by physical treatments; and (*2*) the bands are found in the spectrum of the polymer in all the three phases: liquid, smectic,* and crystalline. The number of bands in the spectrum of the melt or in solution is usually larger than that in the crystalline phase. This fact is due to the possible

* For a discussion on the smectic modification see Natta et al.[9]

existence of more than one rotational isomer in the amorphous phase, whereas only one is preferred in the crystalline state.

Rotation around a C—C bond gives rise to *trans* and *gauche* rotational isomers which are very common structures occurring in the polymer molecules. The doublet at 1450 and 1435 cm.$^{-1}$ observed in the infrared spectrum of *trans*-1,4-polybutadiene in solution in tetrachloroethylene[10] is typical of *trans-gauche* conformational bands. Conformational bands are also found in the spectrum of poly(ethylene terephthalate).[1,11]

In the same class of bands we also include some of the absorptions which are related to the hydrogen-bonded structures of some polymers containing O—H groups. It has been proposed that the 1141 cm.$^{-1}$ band in the spectrum of poly(vinyl alcohol) may be associated with an intramolecular hydrogen bond between two neighboring OH groups.[1]

We are well aware of the fact that many different kinds of conformations are possible in polymers and that the present classification may be too general. However we feel that more theoretical as well as experimental work needs to be done in order to improve our knowledge on these structures before we can proceed to a detailed assignment of the infrared bands to a specific rotational isomer. Consequently we think at the moment a subclassification of these bands is not feasible.

Stereoregularity Bands

One or more bands in the infrared spectrum of a polymer may be called "stereoregularity bands" if: (*1*) with the help of the existing spectral correlations (or with some new ones eventually found with the study of model compounds) they can be associated with well defined atomic configurations which can be transformed to another form only by chemical reaction (i.e., by breaking the chemical bond); and (*2*) they occur in the same number in the spectrum of the polymer in all the possible phases.

The bands commonly used for the determination of the tacticity of a polymer belong to this class. The bands at 699 cm.$^{-1}$ for isotactic 1,2-polybutadiene, at 671 cm.$^{-1}$ for syndiotactic 1,2-polybutadiene,[6] at 843 cm.$^{-1}$ for isotactic 1,4-*cis*-polypentadiene-1,3 and at 833 cm.$^{-1}$ for syndiotactic 1,4-*cis*-polypentadiene-1,3[12,13] may be taken as examples of stereoregularity bands. More work is in progress on isotactic and syndiotactic polypropylene.[14]

In view of the definition of stereoregularity bands we must include into this class also the absorptions associated with the *cis–trans* structures of polymers containing double bonds as in the case of poly-diolefins.[6,15]

The practical importance of the qualitative and quantitative information which can be obtained from the conformational and stereoregularity bands is well known. However spectral correlations cannot be used if one wishes more detailed knowledge of the molecular dynamics of the polymers. For example, the infrared spectra of isotactic polypropylene or of orthorhombic polyoxymethylene cannot be interpreted on the basis of a simple group frequency analysis.

REGULARITY BANDS

Let us take a polymeric chain made up of an infinite number of chemical units organized into a regular helix.* Let us assume at the moment that the chain is isolated from the other neighboring chains. The dynamics of such a system have been studied by several authors.[16-21] The necessary condition that some of the infinite normal modes of vibrations of the infinite chain be infrared-active is that all the equivalent atoms in the various repeating units oscillate in phase.[16] The knowledge of the phase difference between adjacent vibrating units necessarily requires that we may reach each unit by means of screw-symmetry operation along the axis of the chain. The existence of such a covering operation requires that the structure of the helix be rigidly regular. We may then say that the chain is regular when a screw-symmetry operation along the chain axis exists which brings one chemical unit into an equivalent one at a well defined distance.

For a regular chain, infrared-active fundamentals are those which correspond to the motions with phase difference $\delta = 0$ and $\delta = 2\pi/n$, where n is the number of chemical units in the identity period. These selection rules show that the vibrational spectrum of the chemical units coiled into a regular helix may be drastically different either from the spectrum of the isolated unit or from that of an irregular, randomly coiled chain. The spectrum of a regular polymer depends only upon the intramolecular coupling of the oscillations of the various atomic groups.

Moreover, it is well known that the regular structure of the chain, in first approximation, is deformed or destroyed when the compound is melted or dissolved.

We then define as "regularity bands" those bands which, practically, disappear from the spectrum upon melting.† The occurrence of those bands in the infrared spectrum of a polymeric material gives an indication that the polymer is regular.

The theoretical treatments previously mentioned have always dealt with a hypothetically infinite, isolated polymer chain. In practice the polymer is not infinite but it bends, folds and twists,[22-24] depending on the thermal and mechanical treatments to which it is subjected. A distribution of segments of varying lengths exist in a sample. One has then to assume that the length of the various regular segments must be sufficient to approach the selection rules of an infinite chain. No definite data are yet available on the problem of how long a segment should be to give rise to regularity bands.

It has been suggested that some of the bands which may be assigned to regularity in isotactic polypropylene do not completely disappear from the spectrum upon melting, but are only weakened.[25] This problem, which

* Depending upon the helical parameters, the chain may take a planar zigzag form or any other structure which is regularly repeated along the chain.

† Regularity bands may either look like new peaks arising from a region with no absorption or like sharp peaks arising from broad bands observed in the molten sample.

brings into discussion the structure of the polymer in a molten state, will be treated in a future paper.

A typical example of a set of regularity bands may be found in the case of the smectic modification* of isotactic polypropylene.[9] The existence of such a modification has been established for quenched polypropylene by a comparison of the data obtained from x-ray, infrared, density, and NMR measurements.[26] More recently, the same modification has also been postulated on the basis of x-ray and infrared data for polypentadiene and polyhexadiene.[27] It is generally believed that in this form all the individual chains have the helical structure (near-range order) but there is no lateral order sufficient to permit the form to be called crystalline.[9]

If we assume that the random interactions of the neighboring chains in this state have little effect on the dynamics of the helix we can consider the molecule as an isolated entity. We should then find a set of unperturbed regularity bands corresponding to motions with phase difference $\delta = 0$ and $\delta = 2\pi/3$. The proof that those bands are actually due to regularity can be obtained when the screw operation is somehow destroyed. This is obtained by (*a*) changing the geometry of the chain upon melting or (*b*) by changing the nature of some atoms in the chain by means of a synthesis of a deuteropropylene/propylene copolymer. In the latter case the geometry of the helix should not have changed. These theoretical expectations agree with the experiment.[28,29] However, more work needs to be done on the deuterated copolymers.

Whereas the identification of regularity bands in the infrared spectrum is easy, their assignment is more difficult. The precise origin of such bands can be determined only by a rigorous normal coordinate calculation of the whole chain without any simplification or approximation. Only recently, with the aid of large electronic computers, several calculations have been successfully carried out on isotactic and syndiotactic polypropylene and on polyethylene.[30,31]

CRYSTALLINITY BANDS

In the previous discussion on regularity bands we have assumed that the regular chain is independent of its surroundings. In practice many of the synthetic polymers can be packed into a three-dimensional regular structure.[8] The existence of a crystal lattice indicates that mutual interactions between the various chains takes place. The force field acting on the polymer molecule has a well defined symmetry which depends on the type of lattice obtained during the crystallization process. The crystalline state of a polymeric material has been recently studied by various authors.[8,22–24] The situation of the solid state of the polymer which is likely to be close to reality can be described as crystallites of various sizes, not homogeneously distributed, embedded in voids or in an amorphous substance. This definition agrees with the views recently suggested by Lindenmayer,

* Other authors term this the paracrystalline[23] or non-crystalline[26] modification.

Hoseman, and Wunderlich.[22-24] The necessary condition for a regular packing of a polymer chain into a crystal lattice is that the chain is regular.[8] We can then predict that in the infrared spectrum of a crystalline polymer regularity bands must occur.

Moreover, interchain effects may sometimes give rise to vibrational perturbations which have been observed for several molecular crystals[32] and for a few single polymers.[33,34] Static field effects will produce frequency shifts, whereas correlation field splittings may increase the complexity of the observed spectrum. Line, site, and factor group analysis[1,17,19] allow the splitting and the activity of the vibrational transitions of a crystalline polymer to be predicted. The amount of splitting obviously depends upon the intermolecular coupling between the internal coordinates which are mainly involved in a given normal mode. Moreover correlation field splitting will occur only if the unit cell contains more than one chain.

We now make the following assumptions: (*a*) the size of the crystallites in the materials to be studied is large enough to satisfy the Born cyclic lattice conditions;[35] (*b*) the contact between the crystallites and the amorphous part in which they are embedded has no effect on the normal vibrations of the crystalline part.

Some of the bands observed in the infrared spectrum of polymeric substance may be called "infrared crystallinity bands" if: (*a*) x-ray diffraction data prove that the material is crystalline; (*b*) the bands disappear on melting; (*c*) other infrared studies (such as solid solution in isomorphous matrices or isotopic dilution) show that the bands depend upon the existence of a crystal lattice; (*d*) group theory predicts the possible existence of such bands. This definition of crystallinity bands, though very restrictive, seems to us very clear. The occurrence in the spectrum of some bands which satisfy the previous definitions make us sure that the compound is regular and crystalline.

True crystallinity bands have been found for the orthorhombic modifications of both polyethylene[18] and polyoxymethylene.[24]

Unfortunately, very few cases of true crystallinity bands are known in the literature. Most of the polymers which have been found to be crystalline by x-ray measurements show bands in the infrared which do disappear upon melting. However until the dependency of those bands on the crystal lattice has been proved, they tell us only that the polymer is regular; in other words, they are only regularity bands.

ISOMORPHIC PHENOMENA

An application of our classification may be found in the case of the infrared spectra of polymeric isomorphous molecules. Natta et al.[36,37] have recently shown that two main types of isomorphic phenomena may be found for linear macromolecules: (*a*) chain isomorphism involves a solid solution of macromolecules obtained by cocrystallization of different polymers, at least one of which is crystallizable by itself; (*b*) isomorphism of

monomeric units occurs when monomeric units of a different structure are statistically introduced along the chain of a crystallizable polymer without hindering the crystallization of the resulting copolymer, but causing variations of some lattice constant. Monomeric units are linked by covalent bonds and may not be separated by physical means.[36]

It is immediately clear that in the former case we should observe only regularity bands due to the regular chains of the two polymers which are cocrystallized. The spectrum we expect should be practically the same as that of a mechanical mixture of the two single polymers. In the latter case the features of the infrared spectrum should depend upon the composition. As long as the comonomer content is low, fragments of regular chains might exist which are long enough to give regularity bands. To be rigorous some of the regularity bands found in this case should show slight changes due to the perturbing influence of the different comonomer units directly linked to each other. The vibrational perturbation should be analogous[1,38] to the endgroup effects observed for long hydrocarbon molecules or for very short polymer chains. If the comonomer content increases, the chain fragments become very short, the perturbation effect of the neighboring different comonomer units become predominant, and the regularity of the chain is destroyed. Moreover no covering symmetry operation exists. The predicted spectrum should be that of an irregular chain. An explanation of this kind was already suggested by Natta.[37]

In no case are crystallinity bands due to interchain interactions expected. Several experimental observations on copolymers agree with these expectations, as has been shown by Natta et al.[36,37]

The same type of problem may be found in the prediction of the infrared spectra of stereoblock molecules[36] where we should find stereoregularity bands due to tacticity first, and eventually regularity bands when the stereoblocks become long enough for a satisfactory phase coupling.

CONCLUSION

From the previous discussion it turns out that the differences observed in the infrared spectrum of polymeric materials may originate: (*a*) from a well defined spatial conformation of some group of atoms of the chemical repeating unit; (*b*) from the spatial rearrangement of the whole set of chemical units into a regular chain; (*c*) from the packing of the regular chains into a crystal lattice. For each one of these situations we have suggested a classification which can be helpful for the characterization of the polymer.

Dynamic effects which are supposed to be localized in certain points of the polymeric chain give rise, by empirical correlation, to conformational and stereoregularity bands. Regularity bands originate from the intramolecular coupling, whereas intermolecular interactions give rise to crystallinity bands.

With the present classification one can better understand only some of the

bands found in the spectrum. Obviously we do not want to suggest a name for every band of the spectrum. However the occurrence of some of those bands can give us very useful information on the crystallinity, structure, and conformation of the substance we are studying. Moreover quantitative analytical determinations carried out with the use of those bands may provide the chemists with more useful data for their synthesis. In particular, analytical determinations involving crystallinity bands should in principle be comparable with the data obtained from x-ray diffraction studies.

We feel that some confusion exists in the literature. The words atactic, irregular, and amorphous as well as tactic, regular, and crystalline have been respectively used as synonyms. We hope that the present classification may help in making the concepts clear.

We are very grateful to Dr. T. Shimanouchi for his helpful suggestions on the classification discussed in the present paper.

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Discussion

T. Shimanouchi (*Tokyo University, Tokyo, Japan*): When dealing with polymers or fibers very often one suggests that some of the bands observed in the infrared spectrum may be due to crystallinity. Sometimes one does not know the origin of those bands. It seems to me that with the definitions suggested by Dr. Zerbi we can now define the bands due to crystallinity. I would like to comment that as soon as a classification of crystallinity bands is proposed it will be taken up by many high polymer chemists. In fact such a classification is very important in the field of pure and applied science. For this reason I think one has to be very careful about the nomenclature. I am especially concerned with the definition of conformational bands because I think there are very many conformations and possibly many conformational bands.

G. Zerbi: I agree with Dr. Shimanouchi on the problem of the classification of the conformational bands. I should like to point out that our classification is based mainly upon the information we can get only from the infrared spectrum. We feel that at the moment we do not yet have enough information for a subclassification of conformational bands in terms of the many possible conformations one can find in polymers. I think that it should be better at the moment to collect all the bands which may be related to conformational isomers into the same class. When more correlative as well as theoretical studies are available one will then distinguish between various conformational isomers.

T. Miyazawa (*Osaka University, Osaka, Japan*): I would like to point out some of the observations made by Dr. Nielsen on the various crystalline modifications of chain hydrocarbons. For such long chains in a temperature range of about 5°C. just below the melting point we do have a crystalline state but we do not observe the CH_2 rocking splitting at about 720 cm.$^{-1}$. By lowering the temperature just below the transition point suddenly we can see the splitting. In the modification stable at high temperature the molecules are in a crystalline environment but yet they exhibit an absorption around 720 cm.$^{-1}$ that is so close to the band observed for the liquid. Nevertheless we are quite certain the chains are in the regular conformation. Should one call that a crystallinity or a regularity band?

G. Zerbi: Unless we are able to prove that the position of that band in the spectrum depends upon the existence of a crystal lattice, we can only say that the polymer is regular.

S. Krimm (*University of Michigan, Ann Arbor, Michigan, U.S.A.*): I think in that case it is well known that the crystal structure changes as it goes from the orthorhombic to the hexagonal form as a result presumably of rotations around the long chain axis. This fact raises a very interesting point. In fact in that case there is only one band presumably because there is now only one chain per unit cell. How do their frequencies compare? Because one is like a paraffin chain in a deutero-paraffin environment in an orthorhombic cell, the other one presumably is still a planar zigzag extended chain in an hexagonal cell. Of course we do not know how rigid it is. It may be undergoing torsions around its axis to a greater extent, but still it is in a different environment. Dr. Nielsen do you remember what that frequency is?

J. R. Nielsen (*University of Oklahoma, Norman, Oklahoma, U.S.A.*): When the temperature is raised above the transition point one gets, as Dr. Miyazawa has told us, a single band very close to 720 cm.$^{-1}$. In this case the band belongs to the crystalline phase, but because of the rotation or the molecules, or perhaps a partial rotation, the interaction which usually gives rise to the splitting is destroyed and one gets only one frequency.

I would like to ask Dr. Zerbi one question. What evidence there is for forms of polyethylene other than the crystalline and the amorphous?

G. Zerbi: In answer to Dr. Nielsen's question I can only say that while we were writing our paper we have found a short note (W. P. Slichter, in *Growth and Perfection of Crystals*, Doremus, Ed., Wiley, New York, 1958, p. 565) which said that polyethylene exists in a paracrystalline state. If it is true we should like to get the infrared spectrum of that form.

S. Krimm: On the first point that Dr. Nielsen made, it might be worthwhile to go back then to paraffins and polyethylene and look at the details of the doubts and singlets. My recollection is that in the mixed crystals the single band which is obtained is almost midway between the two components. If Dr. Nielsen's recollection is that it is nearer 720 cm.$^{-1}$ in the transition form it means that there is a small difference between these two modifications which might indicate, at least to begin with, a difference in the static field effect.

J. H. Schachtschneider: (*Shell Development Co., Emeryville, Calif., U.S.A.*): I have just one comment with respect to the problem of chain length for regularity bands suggested by Dr. Zerbi. We have recorded the spectra of extended normal paraffins up to C_{20} and have plotted the CH_2 rocking-twisting modes series which terminates at 720 cm.$^{-1}$ (see ref. 38 of this paper). For the in-phase motions the frequency comes down to 720 cm.$^{-1}$ at about 4 or 5 carbon atoms. This is probably not long enough to account for a regularity band because one has to get to some length where the selection rules are essentially those of an infinite chain. For a chain of 4 or 5 carbon atoms the intensities of the other bands which one expects are still noticeable. I would guess that at about 30 carbon atoms the intensity of all the other bands are getting very weak compared with that of the limiting mode at 720 cm.$^{-1}$. This is practically the case of the polymer spectrum where you do not see any other band except the regularity band at 720 cm.$^{-1}$ due to the in-phase motions.

S. Krimm: In this connection I should like to ask a question. Suppose you had some of the shorter chains mixed together. Would you expect some sort of smearing out in the higher frequency region with a sort of addition at 720 cm.$^{-1}$ which would give the appearance of only one band and the other members having disappeared? Has anyone looked at a not-too-crystalline polyethylene at liquid nitrogen temperature to see whether the bands at higher than 720 cm.$^{-1}$ become sharper? I know there was examination of polyethylene at one time at liquid helium temperature but I can only recall that the 720 cm.$^{-1}$ region was shown. The doublet at 720 cm.$^{-1}$ had sharpened up. I do not know if anyone else has really studied the remainder of the spectrum as one goes down in temperature.

T. Miyazawa: In their experiment Drs. Snyder and Schachtschneider have observed very narrow bands for chain paraffins. I also, as well as Dr. Nielsen, have recorded some spectra at liquid nitrogen temperature. But if we measure the infrared absorption of

the higher members at room temperature, say around 50°C., then the bands lying at around 800 or 900 cm.$^{-1}$ are rather diffuse and the peak intensity is rather low.

In these considerations I think $\partial\nu/\partial\delta$ is a very useful quantity. For example, near 720 cm.$^{-1}$ we have found that $\partial\nu/\partial\delta$ is very nearly zero, but near 900 cm.$^{-1}$ it is rather large. For a chain segment of n methylene groups, δ assumes values near $k\pi/n + 1$ with $k = 1,2 \ldots n$. The smallest of these $\pi/n + 1$, thus will correspond to a frequency near 720 cm.$^{-1}$ for segment having a wide distribution of n. Thus the intensity of the 720 cm.$^{-1}$ band is explained. On the other hand the frequencies of bands near 900 cm.$^{-1}$ are much more dependent on n and hence will tend to be smeared out for a collection of segments.

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Vibrational Spectrum of a New Crystalline Modification of Polyoxymethylene

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It has been recently shown that polyoxymethylene (POM) may exist in two crystalline forms, namely hexagonal and orthorhombic. Whereas several extensive works have been carried out on the structure and the vibrational spectrum of hexagonal polyoxymethylene,[1–7] very little is yet known on the structural and vibrational properties of the orthorhombic modification.

For hexagonal POM, x-ray diffraction studies have shown that each unit cell contains one polymer chain.[8–10] The repeating unit of the chain is made up of 9 chemical units coiled into a 5-turn helix with an identity period of 17.3 A.* The isolated chain belongs to the space group $D_{10}\pi/9$. Under suitable conditions of polymerization CH_2O may give polymers either of low or high molecular weight which crystallize into an orthorhombic lattice. This structure has been predicted by Liquori from a conformational analysis.[11] Carazzolo in a very recent paper discusses the detailed results of an x-ray diffraction study.[12] The orthorhombic unit cell contains two polymer chains, each of which contains two monomeric units. The type of chain according to Bunn's notation can be described as B_4 or C_4.

In Figure 1 the arrangement of the polymer chain in the orthorhombic crystal lattice is shown by the projections onto planes *ab*, *bc*, and *ac*. Carazzolo[12] has pointed out that the orthorhombic form of POM must be made up of isomorphous chains without the possibility of alternation or vicariance between right-handed and left-handed helices.[13] For comparison we have collected in Table I some of the structural parameters of both modifications.

EXPERIMENTAL

Orthorhombic POM was first obtained by Bezzi by polymerization of a slightly alkaline solution of CH_2O at a very slow rate.[14] Low molecular

* In a very recent paper Carazzolo[10] discusses the existence of a 29/16 helix and suggests that the structural determinations on the 9/5 hexagonal model with periodicity of 17.3 A. are inaccurate. His new data do not affect the conclusions of the present work.

TABLE I
Structural Parameters of Hexagonal and Orthorhombic Modifications of Polyoxymethylene

	Hexagonal[a]	Orthorhombic[b]
COC and OCO angles	110° 53′	112° 41′
CO distance, A.	1.43	1.43
Internal rotation angle	77° 23′	63° 41′
Identity period, A.	17.3	3.56
No. of polymer chains per unit cell	1	2
No. of monomer units per identity period	9	2
No. of turns per identity period	5	1

[a] From data of Carazzolo.[10]
[b] From data of Carazzolo and Mammi.[12]

weight orthorhombic POM has also been obtained[15] under similar experimental conditions but with concentrated solutions of formaldehyde (paraform). In both cases materials with a large content of orthorhombic POM were obtained (>95%).

The physical properties of this form of POM differ drastically from those of the hexagonal form. Orthorhombic POM is less stable than the hexagonal modification. At 75–80°C. it is transformed into the hexagonal form by an endothermic, monotropic transition. This thermal unstability makes it practically impossible to obtain oriented samples of the orthorhom-

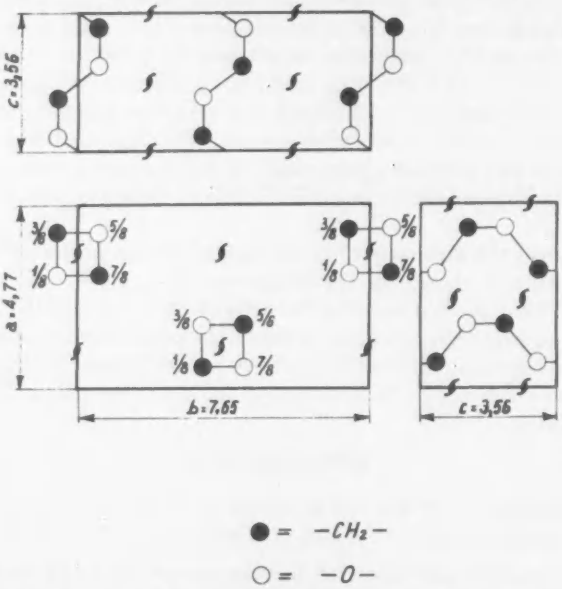

Fig. 1. Crystal structure of orthorhombic polyoxymethylene. Projections onto planes *ab*, *bc*, and *ac*.

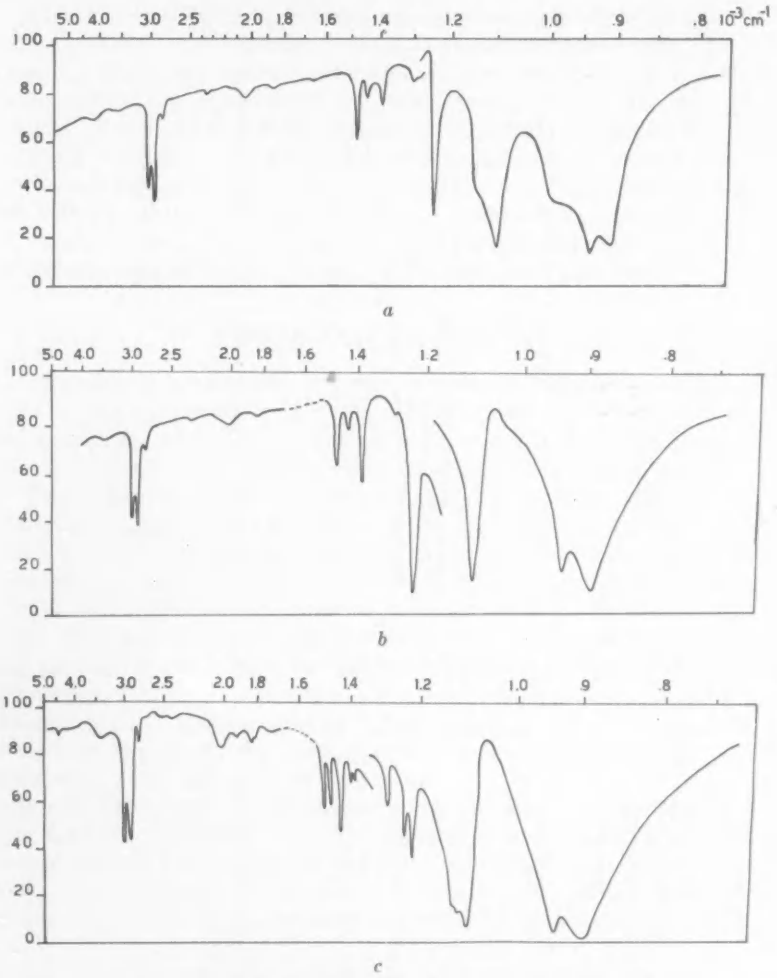

Fig. 2. Infrared spectra of polyoxymethylenes from 5000 to 850 cm.$^{-1}$: (*a*) 30% amorphous; (*b*) hexagonal; (*c*) orthorhombic.

bic form by thermal or mechanical treatments. For this reason we have never been able to carry out any study with polarized light on oriented samples. The hexagonal form obtained from the orthorhombic one shows a very high degree of crystallinity which is determined by x-ray measurements to be greater than 95%. This is confirmed by its high melting point (192–195° C. with decomposition).

Infrared spectra of both the orthorhombic and hexagonal highly crystalline POM have been obtained on Nujol or hexachlorobutadiene mulls with

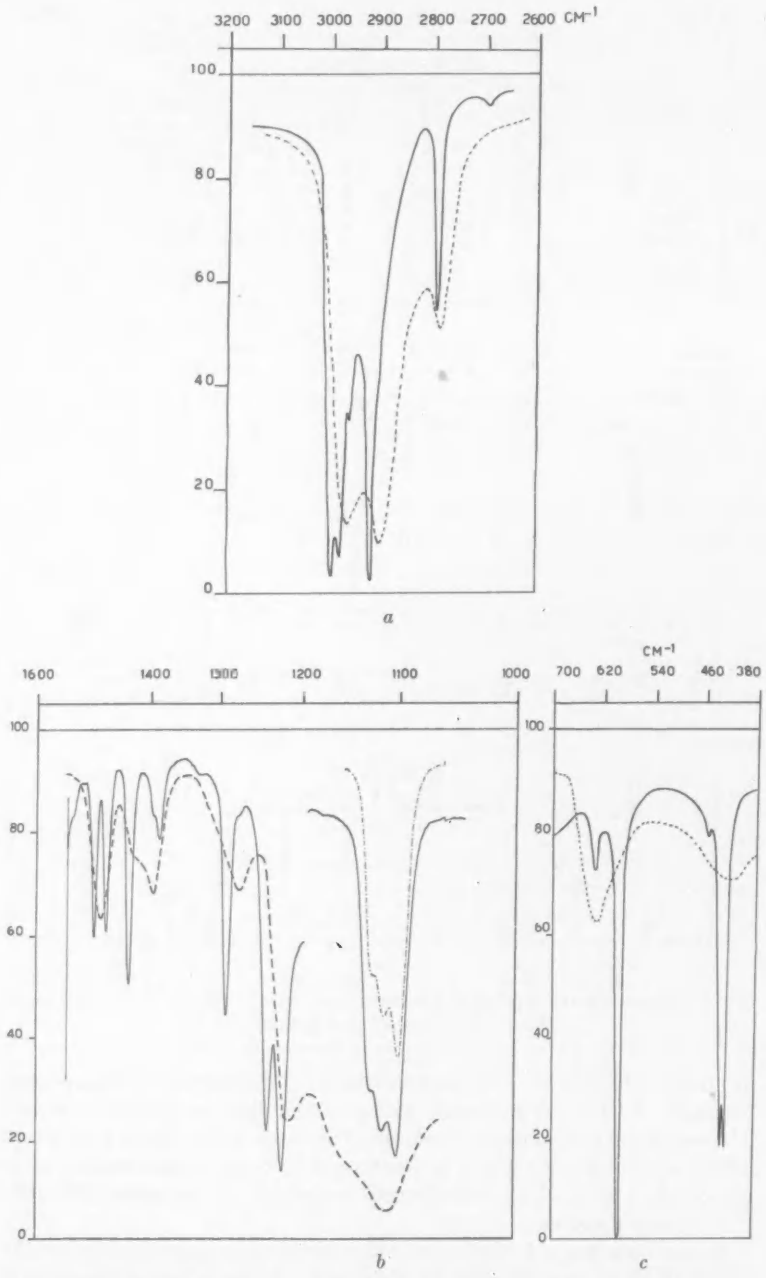

Fig. 3. Details of the infrared spectra of polyoxymethylenes: (- - -) amorphous and (——) orthorhombic: (*a*); 3200–2600 cm.$^{-1}$; (*b*) 1600–1000 cm.$^{-1}$; (*c*) 700–380cm.$^{-1}$

Perkin-Elmer model 21 and 125 spectrometers. The partially amorphous samples have been examined as Nujol mulls or as pressed films. In recording the spectra of the molten samples, acetylated POM or dimethyl ketene–POM copolymers were used. The amount of comonomer was only 2–3%. The infrared spectrum of orthorhombic POM in the region of 5000–650 cm.$^{-1}$ is shown in Figure 2. In the same figure for comparison we also reproduce the infrared spectrum of a partially amorphous hexagonal POM, as well as that of the almost pure crystalline hexagonal modification.

Figure 3 shows some details of the infrared spectrum of orthorhombic POM superimposed on the spectrum of the amorphous substance.

VIBRATIONAL ASSIGNMENT

The identity, a two-fold screw axis and two twofold axes bisecting the $O\hat{C}O$ angles and perpendicular to the C_2' are the symmetry elements of the hypothetically infinite and isolated polymer chain. The factor group of this line group[16] is isomorphous to the D_2 point group.

The 20 normal modes of the isolated chain will be distributed into the various symmetry species as follows: $5A + 5B_1 + 5B_2 + 5B_3$. Of these, the $5A$ modes will be infrared-inactive, the B_1 modes give rise to a transition moment parallel to the helix axis which we take as the z axis. The B_2 and B_3 modes give rise to transition moments perpendicular to the helix axis. Passing to the crystal, the factor group operations of the space group are the identity and three mutually perpendicular twofold screw axes. The factor group is isomorphous to the point group D_2 as in the case of the isolated chain. Of the four factor group operations, E and $C_2(z)$ are the symmetry operations which leave the axis of the chain invariant. The site group is isomorphous to the C_2 point group.

We can then predict (Table II) that each of the line group modes should split into two components when two polymer chains are placed into the crystal lattice. Only one of the components of the doublet arising from the A and B_1 line group modes will be infrared-active. Both components arising from B_2 and B_3 line group modes will be infrared-active. The dichroic behavior which could be easily predicted will be of no help in the present vibrational analysis, owing to the lack of any experimental data on measurements with polarized light.

TABLE II
Correlation Table for the Vibrations of Crystalline Orthorhombic Polyoxymethylene

Line group	Site group	Space group
A		A (R)
B_1	A (T_z)	B_1 (IR, R)
B_2	B (T_x, T_y)	B_2 (IR, R)
B_3		B_3 (IR, R)

The infrared activity of the factor group combinations and overtones can be obtained by the usual methods. All the odd overtones of infrared fundamentals are infrared-active, whereas all the even overtones of the same fundamentals are infrared-inactive. All the binary combinations of infrared fundamentals which are more likely to occur in the traditional frequency range of the vibrational spectrum are infrared-active. All the B_1, B_2, and B_3 fundamentals may also give rise to infrared-active binary combinations with the A Raman active modes. In the present work we did not consider any combinations and overtones of nonfactor group modes which in principle can be infrared-active.[17] Such bands have not been unambiguously found in the polymer spectra.[18]

B_2 and B_3 Line Group Fundamentals

Until other data are available, the assignment of a band to a B_2 or B_3 line group fundamental is somehow arbitrary. For this reason we like to discuss both species together. As expected both B_2 and B_3 line group modes should split into a doublet in the case of the crystal, provided that the intermolecular coupling constants are large enough to produce an appreciable separation of the two vibrational levels. Passing from the amorphous to the orthorhombic crystal, several cases of splitting are actually observed, as shown in Figures 2 and 3. In the C–H stretching region with a grating spectrometer we find two bands for the amorphous and hexagonal form and at least four peaks in the spectrum of the orthorhombic POM. There is one strong doublet at 3000 and 2980 cm.$^{-1}$, a weak shoulder at 2965 cm.$^{-1}$, and a single strong peak at 2920 cm.$^{-1}$. We should expect five maxima arising from one B_1, one B_2, and one B_3 line group modes. Binary combinations of the CH_2 bendings may perturb the frequencies and intensities of the fundamentals occurring in this spectral range. However it seems more reasonable to assign such peaks to the C–H stretching vibrations.

The line group B_3, CH_2 bending* splits into a doublet at 1488 and 1466 cm.$^{-1}$ (hex. 1475 cm.$^{-1}$).

Such a splitting is quite large, and it shows that a strong interaction between the two chains takes place.

Going toward lower frequencies, two bands are found at 1434 and 1381 cm.$^{-1}$. The latter absorption appears like a doublet, but it is very uncertain. Using the supplementary information from the dichroism of the spectrum of hexagonal POM, we must assign the 1434 cm.$^{-1}$ band to the B_2 CH_2 wagging mode. The next pair of frequencies at 1237 and 1220 cm.$^{-1}$ originate from the line group B_2 CH_2 rocking (hex. 1238 cm.$^{-1}$).

Next we find a complex band around 1100 cm.$^{-1}$. We arbitrarily choose

* Obviously the description of the vibrational modes in terms of simplified group frequencies is very approximate. It is commonly known that large couplings of the various internal coordinates do occur even for simpler molecules, especially for vibrations occurring at frequencies below 1300 cm.$^{-1}$ We shall report at a future date on the detailed results of a normal coordinate calculation.

the pair at 1120 and 1110 cm.$^{-1}$ to be the B_3 skeletal stretching + CH_2 rocking mode. The peak observed at 937 cm.$^{-1}$, even if no split is taken to be the B_2 skeletal stretching + CH_2 rocking. We have no evidence for an unambiguous assignment. With regards to the 895 cm.$^{-1}$ band we have experimentally found that it is strongly dependent upon the length of the polymer chain in the case of both the hexagonal and orthorhombic modifications. Its intensity decreases with shortening of the chain and it disappears completely for very low polymers. As we shall discuss in a future paper, this fact may be explained as due to perturbation by the OH terminal group.

The line group B_3, OCO bending mode, has to be assigned to the strong band at 594 cm.$^{-1}$. No splitting is observed, but like other authors[3,7] we feel confident in the choice of this band. It is interesting to notice that the same mode occurs at 630 cm.$^{-1}$ in both the amorphous and hexagonal forms. The lowest observed doublet, at 434 and 428 cm.$^{-1}$, is assigned to the line group B_2 COC bending. Again the corresponding peak in the hexagonal modification occurs at 30 cm.$^{-1}$ higher than in the orthorhombic one. This strong and well defined doublet is a true crystallinity band,[19] which can be used for the study of the crystallization process of the orthorhombic POM.

The downward shift of the last two frequencies by going from the hexagonal to the orthorhombic modification can be explained in terms of the structural changes which take place in the chain (see Table I). Calculations carried out by Miyazawa[6] on a simplified model of POM have shown that these frequencies are very sensitive to the change of the internal rotational angle. The downward shift as observed in our experiments is in accord with what has been suggested by the calculations. In addition to the change of the internal rotation angle, the COC and OCO angles undergo a change which may somehow influence the frequency of the corresponding normal modes. More detailed calculations are in progress in our laboratory.

One more B_3 mode remains to be assigned. Even though it is not split we take the band at 1290 cm.$^{-1}$ as due to the CH_2 twisting mode.

B_1 Line Group Fundamentals

Normal modes belonging to this species are expected to be mainly one C–H stretch, one CH_2 wag, one C–O stretch, one CH_2 rock, and one skeletal torsion. Furthermore theory predicts that only one component of the factor group doublets will be infrared active. Besides those bands discussed in the case of the B_2 and B_3 species, peaks which do not split are observed at 2965, 1380, 1092, and 897 cm.$^{-1}$. We assign them to C–H stretch, CH_2 wag, COC sym. stretch, and CH_2 rock + skeletal stretch, respectively. The torsional mode is expected at frequencies beyond the region of our observation.

Each Raman-active line group fundamental of species A should give

TABLE III
Infrared-Active Fundamental Vibrations of Polyoxymethylene

Appr. mode[a]	Frequency, cm.$^{-1}$ (and intensity) Hexagonal, 70% cryst.[b]	Hexagonal, 95% cryst.[b]	Orthorhombic, 95% cryst.	Line group species
CH stretching	2980 (s)	2984 (s)	3000 (s) 2980 (s) 2965 (m)	B_1, B_3
	2920 (s)	2920 (s)	2920 (s)	B_2
CH_2 bending	1475 (m)	1471 (m)	1488 (m) 1466 (m)	B_3,
CH_2 wagging	1436 (w)	1434 (m)	1430 (m)	B_2
CH_2 wagging	1387 (m)	1384 (m)	1392 (m) 1381 (w)	B_1
CH_2 twisting	1292 (w)	1290 (w)	1290 (m)	B_3
CH_2 rocking + COC bending	1280 (w)? 1238 (s)	? 1238 (s)	(1287) (m) 1237 (m) 1220 (s)	B_2
C—O stretching	1120 (s)	—	1120 (shd) 1110 (s)	B_3
Skeletal stretching + CH_2 rocking	1095 (vs) 975 (sh, s)	1098 (vs) —	1092 (vs) —	B_1
Skeletal stretching + CH_2 rocking	936 (vs)	936 (vs)	937 (vs)	B_2
CH_2 rocking + skeletal stretching	900 (vs)	897 (vs)[c]	895 ± 5 (vs)	B_1
OCO bending	630 (s)	630 (s)	594 (s)	B_3
COC bending	455 (m)	456 (m)	434 (m) 428 (m)	B_2

[a] Our assignments agree with those proposed by Novack and Whalley.[3]

[b] New frequencies obtained with a grating instrument. They are very similar to those reported by Novack and Whalley.[3]

[c] The spectrum of low molecular weight POM shows a band at 910 cm.$^{-1}$.

rise to one infrared-active band in the case of the crystal. No evidence has been found for any of the expected infrared-active components.

In Table III we have collected the proposed assignments for the infrared-active fundamentals.

We are very grateful to Prof. Giulio Natta for the encouraging support to this work and to Prof. S. Bezzi for the gift of a sample of the high molecular weight POM. We thank Dr. G. A. Carazzolo for very helpful discussion on the structure of POM and Prof. E. Mantica and Dr. S. Leghissa for the interest they have shown in our work.

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Sur la Spectroscopie Ultra-Sonore des Solutions de Macromolécules en Chaînes

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I. RAPPEL DE QUELQUES RÉSULTATS DE LA SPECTROSCOPIE ULTRA-SONORE

La Fréquence Caractéristique d'une Macromolécule

On envisage la propagation d'une onde longitudinale (sinusoïdale) de fréquence N dans une solution de macromolécules, et l'on considère le coefficient d'absorption α pour l'amplitude de l'onde. Il est connu que dans un liquide pur α/N^2 = constante loin d'une fréquence de relaxation.

Nombre de macromolécules en solution montrent un comportement particulier consistant en une chute de α/N^2 se produisant à une fréquence bien déterminée N^*. La Figure 1 donne un exemple de ce comportement.[1] Elle concerne une solution benzénique sensiblement monodispersée d'un polystyrène (préparé par la méthode de Szware), de masse moléculaire moyenne en poids (déterminée par diffusion de la lumière) $M_w = 850.000$, à la concentration $c = 4{,}58 \times 10^{-2}$ g./cm.^{3} Au lieu de représenter les variations de α/N^2 en fonction de la fréquence on a porté α_{sp}/c en fonction de N, où l'absorption spécifique $\alpha_{sp} = (\alpha - \alpha_0)/\alpha_0$, α et α_0 étant respectivement l'absorption de la solution et celle du solvant. Les deux représentations sont équivalentes car $\alpha_{sp} = (\alpha/N^2)/(\alpha_0/N^2) - 1$, et ici α_0/N^2 = constante. Les mesures ont été effectuées à l'aide d'un dispositif interférométrique[1,2] permettant d'explorer à fréquence continûment variable certains domaines de la bande de fréquence envisagée (0,8–27 Mcycle/sec). Il a été vérifié que: (*a*) le coefficient d'absorption de la solution est indépendant de la puissance acoustique délivrée; (la puissance électrique maximum au transducteur produisant les ondes acoustiques était de l'ordre de 10^{-4} w/cm.^{2}; sa valeur minimum était environ 100 fois plus faible).

Aussi, (*b*) la valeur de l'absorption d'une solution est indépendante de la durée de l'irradiation ultra-sonore antérieure, quelles que soient les fréquences de mesure et d'irradiation antérieure choisies dans la bande indiquée plus haut.

Le phénomène que traduit la courbe de la Figure 1 est surprenant d'un double point de vue. Premièrement du point de vue de l'acoustique, car si les liquides présentant de la relaxation montrent une chute de α/N^2 en fonction de la fréquence, la chute est toujours étalée. C'est ainsi que α/N^2

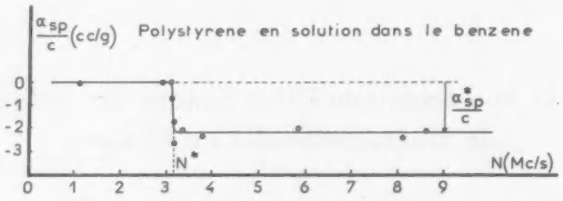

Fig. 1. Spectre ultrasonore d'une solution macromoléculaire montrant la brusque chute de l'absorption à une fréquence bien définie.

varie comme $1/(1 + 4\pi^2N^2\tau^2)$ lorsqu'il s'agit d'un phénomène caractérisé par un seul temps de relaxation τ.

Deuxièmement, le phénomène est également surprenant du point de vue de la physico-chimie macromoléculaire, car une molécule en chaîne est caractérisée par un spectre de temps de relaxation, et l'on conçoit difficilement, au premier abord, qu'elle possède une fréquence caractéristique bien définie.

En fait, l'ensemble des résultats expérimentaux résumé en partie ci-dessous, fait apparaître qu'il ne s'agit pas ici d'un phénomène de relaxation, du moins au sens habituel du terme.

Facteurs Affectant la Fréquence Caractéristique

Les mesures systématiques sur les solutions de polymères vinyliques ont permis de dégager les faits suivants.

La fréquence caractéristique N^* est indépendante de la concentration en polymère[3,4] et indépendante de la nature du solvant.[5] Le fait que la fréquence caractéristique N^* observée en solution soit indépendante de la concentration en polymère conduisait à se demander si un polymère liquide fournit un phénomène analogue à celui que l'on vient de décrire. Des mesures préliminaires sur un échantillon de polyvinylisobutylether d'une masse moléculaire de l'ordre de 5.000 ont fourni une chute de l'absorption ultrasonore aux environs de 3,5 Mcycle/sec, alors qu'une solution benzénique du même produit à la concentration de $3{,}4 \times 10^{-2}$ g/cm³ montrait une chute de l'absorption spécifique à 3,6 Mcycle/sec.

La fréquence caractéristique est une fonction croissante de la masse moléculaire;[3,4] on notera que ce comportement est à l'opposé de celui que l'on attendrait s'il s'agissait d'un processus de relaxation. D'autre part, la fréquence N^* croît lorsque décroît la masse du groupement latéral dans la chaîne vinylique.[5]

Enfin, le spectre ultrasonore dans son ensemble, et la fréquence caractéristique en particulier, sont sensibles à la stéréorégularité.[4,6,7]

La figure 2 résume les résultats obtenus pour une série de polyméthacrylates de méthyle d'origines différentes. Le spectre ultrasonore du polyméthacrylate de méthyle présente dans le domaine de fréquence exploré deux chutes successives de l'absorption. Sur la figure on a porté la

valeur de la première fréquence caractéristique N_1^* en fonction de la masse moléculaire M_w, en coordonnées semi-logarithmiques. A côté de chaque point représentatif on a indiqué, lorsqu'ils sont disponsibles, les résultats des mesures de résonance magnétique nucléaire.

L'indication "iso" signifie que le spectre de RMN présente essentiellement un pic isotactique. Les points représentatifs correspondants sont des carrés.

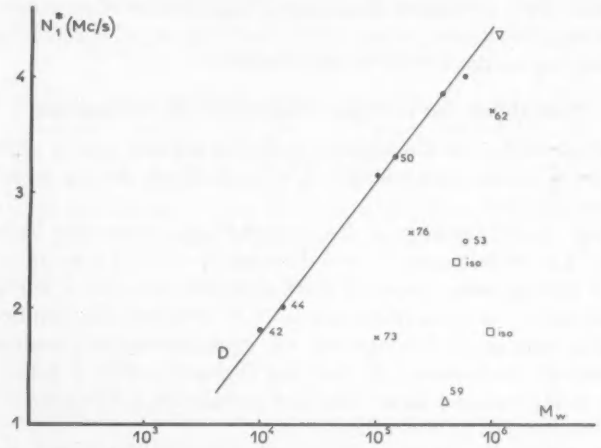

Fig. 2. Première fréquence caractéristique de divers polyméthacrylates de méthyle: (□) pic isotactique sur le spectre RMN; (×) échantillons à prédominance syndiotactique; (●) produits préparés par la méthode de Szwarc dans le tétrahydrofuranne à −78°C à partir du tétramère disodé de l'α-méthylstyrène comme catalyseur; (△) produit préparé par la même méthode à partir du naptalène sodium comme catalyseur; (○) un autre polymère de Szwarc à légère prédominance syndiotactique; (▽) produit préparé par irradiation γ dans l'huile de paraffine à −78°C.

Les chiffres concernent des produits dont les spectres présentent un pic syndiotactique et un pic atactique prononcés, le pic isotactique étant absent ou peu marqué; ces chiffres donnent la surface du pic syndiotactique lorsqu'on a posé égale à 100 la somme des surfaces des pics syndiotactique et atactique. Les échantillons à prédominance syndiotactique sont désignés par une croix.

Les cercles pleins qui se placent au voisinage de la droite D, désignent des produits préparés par la méthode de Szwarc dans le tétrahydrofuranne à −78°C, à partir du tétramère disodé de l'α-méthylstyrène comme catalyseur. Le triangle désigne un produit préparé par le même méthode mais à partir du naphthalène sodium comme catalyseur. Le cercle vide désigne un autre polymère de Szwarc à légère prédominance syndiotactique. Le triangle renversé désigne un produit, dû à l'obligeance de M. Chapiro, préparé par irradiation γ dans un verre d'huile de paraffine à −78°C.

Les mesures ultrasonores concernant ces deux derniers polymères ont été effectuées par Fix.[8]

Les résultats résumés par la figure 2 font apparaître les conclusions suivantes: (*1*) un degré de tacticité élevé (syndiotacticité ou isotacticité) abaisse la fréquence caractéristique N^*; (*2*) toutefois, à masse moléculaire égale, les points représentatifs ne se placent pas forcément dans l'ordre des tacticités RMN (exemple des points "59" et "53" auxquels correspond une valeur anormalement basse de N^*).

Par suite, il est nécessaire d'envisager l'intervention d'un paramètre de structure supplémentaire, autre que la tacticité, et cette conclusion sera confirmée plus loin dans le cas du polystyrène.

Remarques sur l'Origine Moléculaire du Phènomène

L'ensemble des résultats résumés ci-dessus indique que le phénomène observé est d'origine intramoléculaire, et qu'il affecte des segments limités des macromolécules.

Un essai d'interprétation a été présenté[6] qui repose sur l'hypothèse suivante: à basse fréquence (c'est-à-dire pour $N < N^*$) il y aurait vibration forcée de certains segments entre deux configurations 1 et 1′ energétiquement favorisées. A haute fréquence ($N > N^*$) l'énergie de vibration serait telle qu'un changement coopératif de configuration se produise (par franchissement de barrières de potentiel limitant la libre rotation), et la nouvelle configuration 2 aurait alors une population n_2 très grande devant sa population $n_{2,0}$ en l'absence de champ.

Un tel schéma permettrait d'expliquer la brusque variation de l'absorption qui se produit à la fréquence $N = N^*$; il serait compatible d'ailleurs avec une augmentation de l'absorption aussi bien qu'avec une diminution de cette grandeur à la fréquence caractéristique. Le même schéma permettrait de comprendre qualitativement la grande sensibilité de la fréquence caractéristique à la tacticité puisqu'une différence de tacticité modifie le niveaux énergétiques intramoléculaires.

On a tenté de mettre en évidence directement un changement de configuration des molécules en comparant une propriété optique de la solution soumise au champ ultrasonore à deux fréquences, respectivement inférieure et supérieure à la fréquence caractéristique.

On a notamment tenté de mettre en évidence, pour des solutions optiquement actives, une variation du pouvoir rotatoire sous l'influence du champ acoustique, laquelle pourrait présenter des caractères différents de part et d'autre de la fréquence caractéristique.[9] De même, on a essayé de mettre en évidence une influence du champ acoustique sur l'absorption infrarouge des solutions de hauts polymères, mais les résultats de ces diverses expériences ont été négatifs jusqu'à présent.

Tout récemment une expérience a été réalisée sur le principe suivant: on mesure à une fréquence N_1 l'absorption d'une solution de polymères soumise à un deuxième champ ultrasonore de fréquence $N_2 > N^*$. Si l'hypothèse avancée précédemment est correcte, et si le deuxième champ est suffisam-

ment intense, les molécules de polymère doivent subir des changements de configuration tels que le coefficient d'absorption mesuré à la fréquence N_1 soit modifié. Le résultat de cette expérience, sur laquelle on reviendra plus en détail ailleurs,[10] a été négatif, de sorte qu'il sera vraisemblablement nécéssaire de modifier plus ou moins profondément le schéma rappelé ci-dessus.

II. NOUVEAUX RÉSULTATS CONCERNANT LA SENSIBILITÉ DE LA FRÉQUENCE CARACTÉRISTIQUE A LA STRUCTURE LOCALE DU POLYMÈRE

Polystyrène Radicalaire

La figure 3 reproduit des résultats de mesures récentes de Lang[9] concernant les solutions benzéniques de deux polystyrènes de masses moléculaires viscosimétriques 30.000 et 1.350.000 préparés par voie radicalaire avec le peroxyde de benzoyle comme catalyseur; on a représenté le spectre ultrasonore des deux solutions, dont la concentration était voisine de $4{,}5 \times 10^{-2}$ g/cm³, ainsi que le spectre ultrasonore du mélange à parts égales des deux liquides.

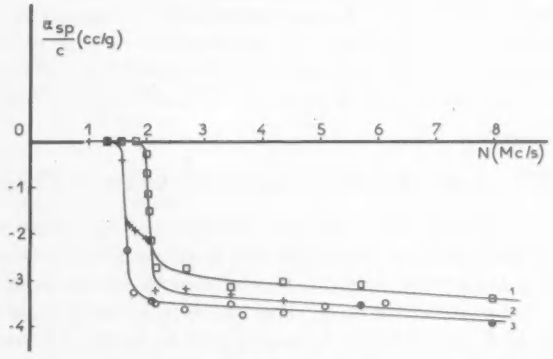

Fig. 3. Spectres ultrasonores de deux solutions de polystyrène dans le benzène et de leur mélange à parts égales: (□) $M_B = 1{,}35 \times 10^6$; (○) $M_A = 30.000$; (+) mélange A/B = 50/50.

Les spectres des deux polymères présentent une chute brusque respectivement à 1,65 Mcycle/sec et à 2,05 Mcycle/sec, et le spectre du mélange présente deux chutes aux deux fréquences précédentes. (Une telle expérience avait déjà été réalisée pour un mélange de deux polystyrènes de masses respectives 3.500 et 220.000, et l'on avait discuté les possibilités d'application du phénomène à l'analyse de polydispersité.[11])

Sur la figure 4 on a porté la fréquence caractéristique du polystyène en fonction de la masse moléculaire en coordonnées semi-logarithmiques. La courbe concerne des polymères préparés par la méthode de Szware,[3,4] tandis que les croix concernent les deux polymères radicalaires étudiés par Lang.[9]

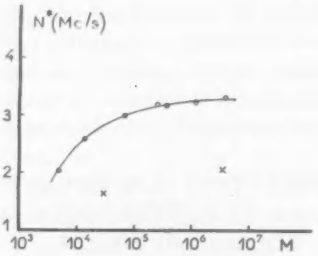

Fig. 4. Fréquence caractéristique de divers polystyrènes: (O) polymères préparés par la méthode de Szwarc; (×) polymères radicalaires étudiés par Lang.[9]

On voit que les fréquences caractéristiques des polymères radicalaires diffèrent notablement, à masse moléculaire égale, de celles des polymères anioniques de Szwarc. Toutefois, il n'est pas probable que les deux procédés de polymérisation envisagés puissent conduire à une différence de tacticité telle qu'elle explique la différence de fréquence caractéristique observée. Il semble donc que des procédés de polymérisation différents puissent conduire à des produits ayant à masse égale, des fréquences caractéristiques très différentes, même si les tacticités de ces produits ne sont pas essentiellement différentes. Le polystyrène radicalaire étant susceptible de présenter un certain taux de ramification, une influence éventuelle de ce dernier facteur sur la fréquence caractéristique N^* doit être envisagée.

Mesures sur des Molécules Brisées par l'Action des Ultra-sons

La grande sensibilité de l'absorption ultrasonore à la structure locale du polymère, révélée par tout l'ensemble des résultats précédents, nous a conduits à nous poser la question suivante: l'influence de la masse moléculaire M sur la fréquence caractéristique N^* dans une série de produits obtenus par le même procédé de polymérisation (exemple de la droite D de la Figure 2), est-elle une influence réelle de la masse moléculaire ou traduit-elle, au moins partiellement, une différence de structure locale des polymères de masses différentes?

Autrement dit: selon que l'on conduit une polymérisation de manière à obtenir un produit de faible masse moléculaire ou un produit de masse moléculaire élevée (en variant par exemple la quantité de catalyseur), les polymères ont-ils ou non la même structure locale?

Pour tenter de répondre à cette question nous avons dégradé diverses molécules de polyméthacrylate de méthyle par l'action d'un rayonnement ultrasonore intense (nous avons utilisé un désintégrateur Mullard 4200) et nous avons comparé la fréquence N^* avant et après la dégradation.

Si la droite D de la Figure 2 traduit un effet réel de la masse moléculaire, les points représentant le polymère avant et après la dégradation doivent se trouver, dans ce diagramme, sur une parallèle à la droite D. Si, au con-

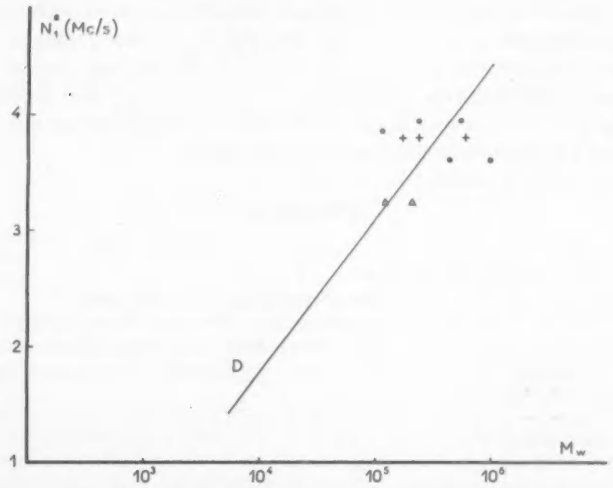

Fig. 5. Première fréquence caractéristique de divers polyméthacrylates de méthyle avant et après dégradation par un rayonnement ultrasonore intense: (●) polymère préparé par voie radicalaire; (○) polymère de Szwarc préparé à partir du tétramère de l'α-méthylstyrène comme catalyseur; (+) polymère de Szwarc préparé à partir du tétraphényl-1,1,4,4-butane comme catalyseur; (△) polymère de Szwarc préparé à partir du diphénylméthylsodium comme catalyseur.

traire, il n'y a pas d'effet réel de la masse, et si seule la structure locale varie en fonction de M le long de la droite D, les points en question doivent se trouver sur une horizontale.

Nous espérons que de telles expériences, en fournissant éventuellement des réponses différentes pour des polymères de préparations différentes, aideront également à déceler le paramètre de structure non encore identifié qui influence la valeur de la fréquence caractéristique N.*

Les résultats d'expériences préliminaires pour divers polyméthacrylates de méthyle sont donnés sur la figure 5. Un produit non dégradé et les produits dégradés correspondants (au nombre de un ou de deux) sont désignés par le même symbole. Dans chaque série, le produit non dégradé est celui qui se trouve le plus à droite sur le diagramme. Ainsi le cercle plein situé le plus à droite désigne un polymère préparé par voie radicalaire. De même le cercle vide, la croix, et le triangle situés le plus à droite désignent des polymères de Szwarc préparés respectivement à partir du tétramère de l'α-méthylstyrène, du tétraphényl-1,1,4,4-butane, et du diphénylméthylsodium comme catalyseurs.

En général la dégradation ultrasonore a réduit les masses moléculaires moyennes à une valeur située entre le tiers et la moitié de leur valeur initiale. Dans un cas M_w a été divisé par 4,5 environ. Il semble résulter de la figure 5 que la dégradation déplace le point représentatif sur une droite voisine d'une horizontale. Cette conclusion devra toutefois être regardée

comme provisoire en attendant qu'une réduction plus importante de la masse moléculaire moyenne ait pu être réalisée, et que l'influence d'une variation éventuelle de la polydispersité par l'effet du rayonnement ultrasonore ait pu être prise en considération.

L'importance de la question soulevée nous a néanmoins conduits à communiquer les résultats préliminaires qui précèdent.

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Infrared Spectra of Amylose and Its Oligomers

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INTRODUCTION

Amylose is the linear component of starch. It is chemically related to cellulose, being similarly constituted of glucopyranose units interlinked by oxygen (glycosidic) bridges. Amylose and cellulose chemically differ from each other in the type of glycosidic bonds. Actually, glycosidic bonds in amylose are of the α type (i.e., they project from the glucopyranose ring on the same side) and in cellulose they are of the β type (i.e., they project from opposite sides of the ring).

It may seem rather surprising, considering the wide natural occurrence and importance of amylose, that very little attention has been paid to it by the spectroscopists. This can be in part explained by difficulties encountered in obtaining adequately characterized specimens and by the limited preliminary structure information thus far available from other physical techniques.

Furthermore, while there is no doubt that in cellulose the glucopyranose rings assume a defined "chair" conformation, which ring conformation is taken by amylose and its derived products is still under discussion.

It is well known that chair forms of unsubstituted cyclohexane and tetrahydropyrane rings are *per se* more stable than the boat type, but substituents on the ring can nevertheless stabilize a boat conformation when molecular strain and nonbonded interactions for it are smaller than in any other possible forms. This has been proposed by some authors to occur in the case of several α-glucopyranosides, including amylose and its cyclic oligomers (cyclodextrins).[1–3]

Of the two possible chair conformations and six boat forms, on the basis of stability considerations only the so-called C1, B1, and 3B, according to the designations of Reeves,[4] were generally taken into account in the attempts to build up amylose or cyclodextrin structure. Figure 1 shows these most stable conformations and the dimeric (maltosidic) units built with them as models for amylose. It can be seen that with C1 and B1 units only helical or cyclic structures can be constructed, while 3B units allow essentially linear chains. We want to stress this point, since the "boat hypothesis" suggests B1 forms for cyclic structures and a conformation between 3B and B1 for extended structures.[1–3]

It must be pointed out that the orientations of the substituents are quite

different according to the particular ring conformation taken into account. C1 rings of α-glucopyranose present all the large substituents equatorially oriented with respect to the plane of the ring, except the C_1—O (glycosidic)

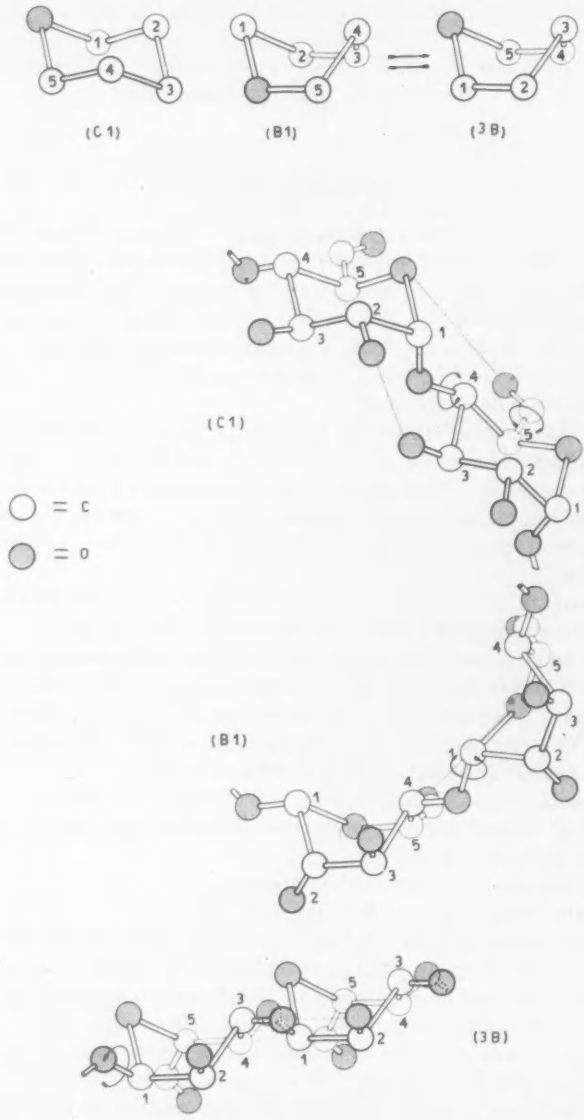

Fig. 1. Most stable conformations of α-glucopyranose ring and maltosidic units built with the above conformations as models for amylose.

bond, which is axial. The corresponding C_1—H (not shown in the figure) is therefore equatorially oriented. Both B1 and 3B α-glucopyranose rings show their glycosidic bonds equatorially oriented with respect to the plane of the ring.

From the above considered structures it is evident that different groups can lie on the internal surface of an amylose helix or of a cycle, depending on the particular conformation of the glycopyranose rings. In connection with studies on interactions in inclusion complexes of amylose and cyclo dextrins we are interested in determining the conformation of glucopyranose rings in the above products. We have therefore investigated the infrared spectra of amylose and its derived products for the purpose of getting information on the conformation of their glucopyranose rings.

For the assignment of infrared bands of amylose, we have considered the known assignments for cellulose.[5-7] We have also taken into account the spectral behavior of more workable model substances such as linear and cyclic oligomers, which are more soluble and crystallizable than amylose. We have also considered the effects of deuteration on the infrared spectra of all the above products.*

Because of our interest in the conformation of the glucopyranose rings, we have devoted attention to a band which seem particularly affected by the stereochemistry of the C_1 group, i.e., of the carbon atom to which the glycosidic bond is attached.

This is the band that Barker and co-workers,[8] in their extensive studies on the infrared spectra of carbohydrates, observed for α-anomers near 850 cm.$^{-1}$ and for β-anomers near 895 cm.$^{-1}$. These bands were found by the above authors to be virtually unaffected by modifications or by replacement of the —O— group at C_1.

RESULTS

1. Crystalline Products

Cyclic oligomers of amylose (cyclodextrins) can occur in a variety of crystalline forms.[9] Eight crystalline modifications of cyclohexaamylose (α-cyclodextrin) have been obtained according to a scheme of Ulmann and co-workers.[10] They are reproducibly convertible with each other and present characteristic x-ray diffraction patterns.†

Figure 2 shows the infrared spectra of four hydrated modifications of cyclohexaamylose. The spectra are somewhat different from each other and show many relatively sharp bands which are often displayed as doublets in regions where α-glucopyranosides, both simple and complex, generally show single bands.

* The spectra were taken with a Perkin-Elmer model 125 grating spectrophotometer. Details on materials and on experimental methods will be given in a subsequent paper.

† The so-called α-5 form contains some ethyl alcohol, most probably included in the ring. Spectra of inclusion complexes of cyclodextrins will be reported elsewhere.

Figure 3 shows the spectra of four crystalline dehydrated modifications of cyclohexaamylose. The reduced splitting and the broadening of the bands in the dehydrated cyclohexaamyloses with respect to the hydrated forms

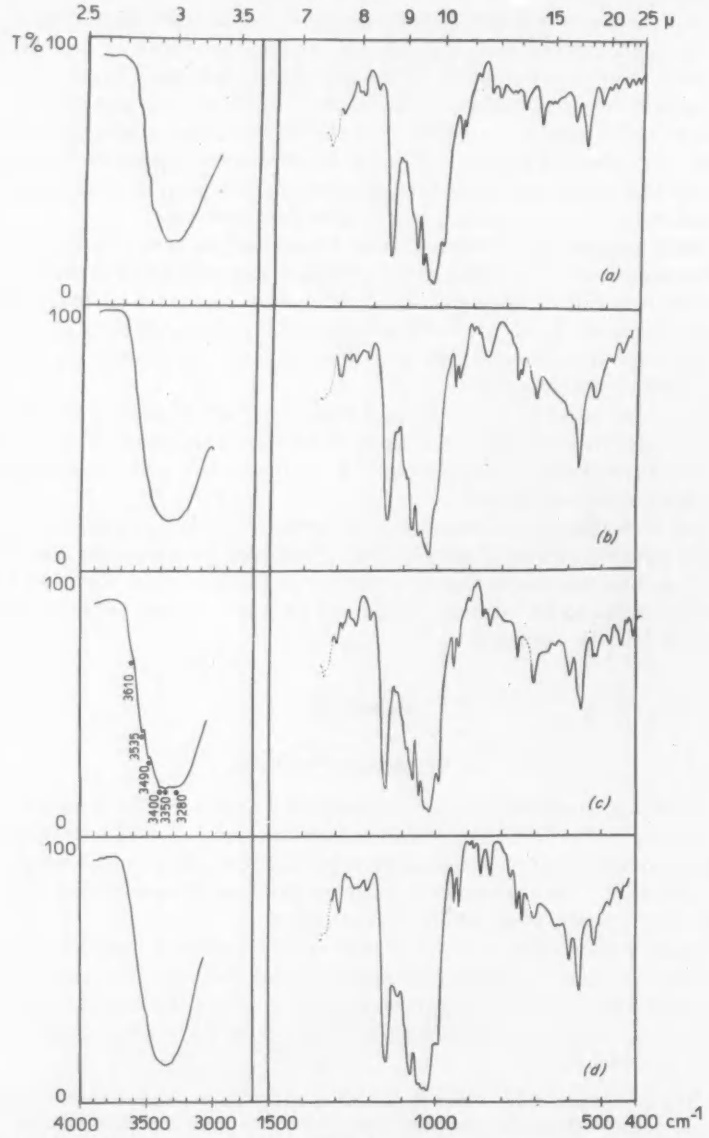

Fig. 2. Infrared spectra of crystalline hydrated cyclohexaamyloses (nujol mulls): (*a*) α_3; (*b*) α_5; (*c*) α_7; (*d*) α_9.

reflect the well known contribution of water molecules to the structures of crystalline carbohydrates.[11]

We are particularly interested in investigating crystallinity effects on the

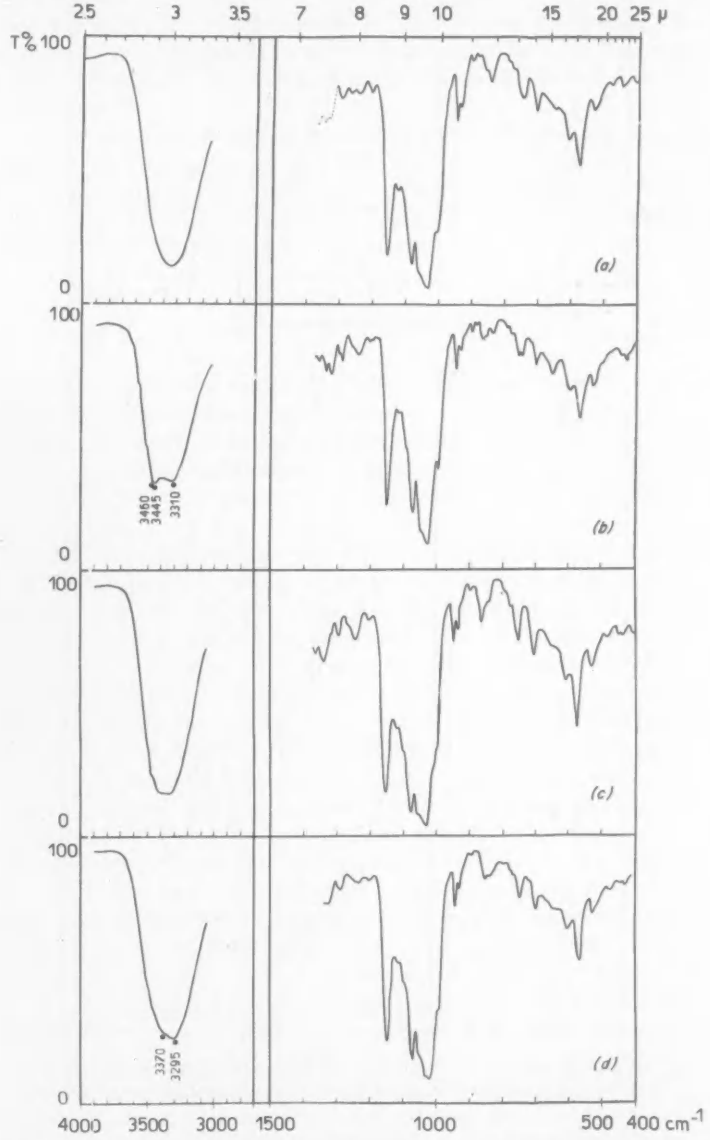

Fig. 3. Infrared spectra of oven dried cyclohexaamyloses (nujol mulls): (*a*) α_2; (*b*) α_4; (*c*) α_6; (*d*) α_8.

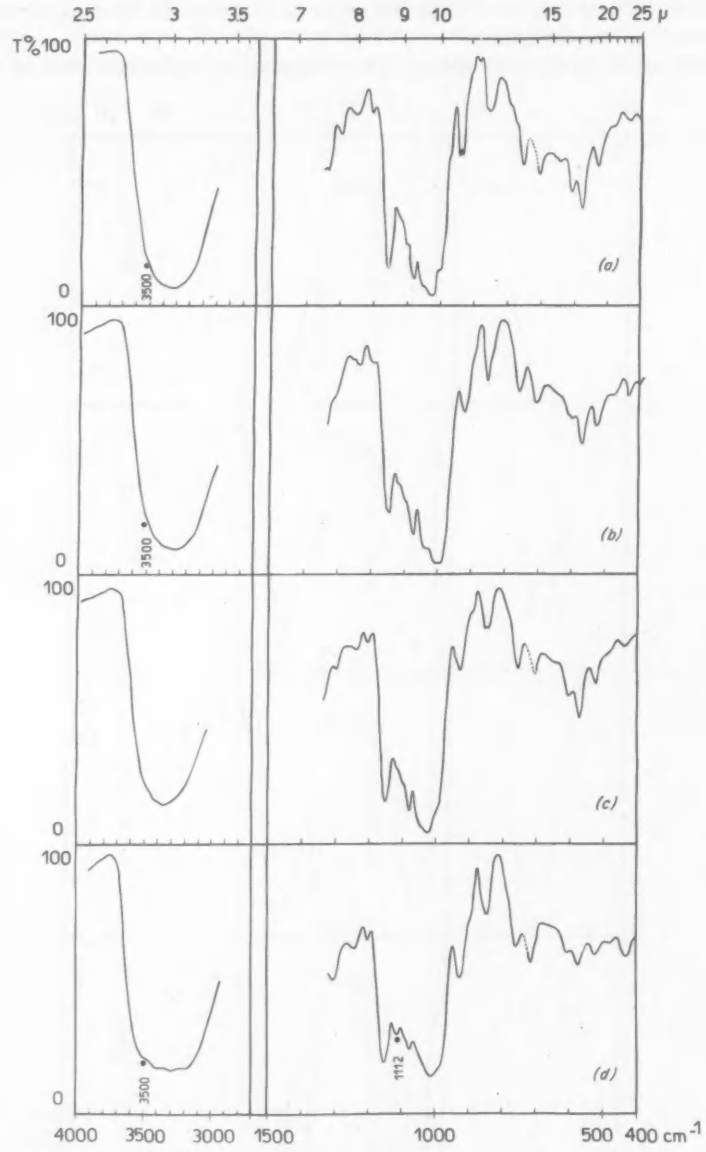

Fig. 4. Infrared spectra of cycloheptaamylose, amylodextrin and amylose (nujol mull): (*a*) cycloheptaamylose; (*b*) amylodextrin; (*c*) V amylose; (*d*) B amylose.

C_1 group absorption mentioned in the introduction. While this band is generally a single band in simple saccharides,[8] in cyclohexaamyloses it is markedly affected by the crystalline form, revealing from two to four component bands.

Figure 4 shows the infrared spectra of crystalline cycloheptaamylose (β-cyclodextrin), amylodextrin (a linear dextrin having a degree of polymerization about 25) and amylose, this latter in the so called V and B modifications.[12]

V and B amyloses display a somewhat different pattern of hydrogen bonded O—H absorption in the 3300–3500 cm.$^{-1}$ range. B amylose shows an additional band a 1122 cm.$^{-1}$. (Further investigation is needed in order to establish if these features are affected by the infrared sampling and by the degree of hydration of the samples.)

2. Amorphous Products

Freeze-drying aqueous solutions of KBr (or KCl) and the saccharide provides the saccharide in the amorphous state.[7,13] Actually, for the low concentrations involved, dissolved saccharide molecules are considered fully solvated. Rapid freezing does not allow the molecules to group themselves in crystallites, and the inclusion in the KBr matrix does not generally allow recrystallization.

Figure 5 illustrates the striking effect of decrystallization by freeze-drying on the infrared spectra of simple α-glucopyranosides such as α-methylglucoside and maltose. Many bands displayed in the crystalline state are damped out in the amorphous spectrum, which assumes the general pattern of a polymer spectrum. Hydrogen-bonding patterns (O—H bands in the 3300–3500 cm.$^{-1}$ region) appear to be greatly affected by decrystallization, just as is to be expected. The large O—H stretching band becomes less broad, and its center moves toward higher frequencies, revealing well reduced intermolecular associations in the amorphous state. Intramolecular hydrogen bonding to which bands upwards of 3450 cm.$^{-1}$ are related[14] is also reduced, as appears from the 3540 cm.$^{-1}$ sharp peak of crystalline α-methylglucoside, which are still shown by the amorphous product but only as a weak inflection. This is understandable, since in crystals some intramolecular hydrogen bond may be stabilized by intermolecular hydrogen bonding involving the same oxygen atoms.

Figure 6 shows the infrared spectra of cyclodextrins, amylodextrin, and amylose in the amorphous state. It is apparent that spectral differences between cyclodextrins, amylodextrin, and amylose are limited to small frequency displacement of some bands. Cyclodextrins still retain somewhat finer details of some bands, namely those in the 850 cm.$^{-1}$ and 925–950 cm.$^{-1}$ regions in respect to amylodextrin and amylose, but infrared spectra of amorphous amylodextrin and amylose are to be considered practically identical.

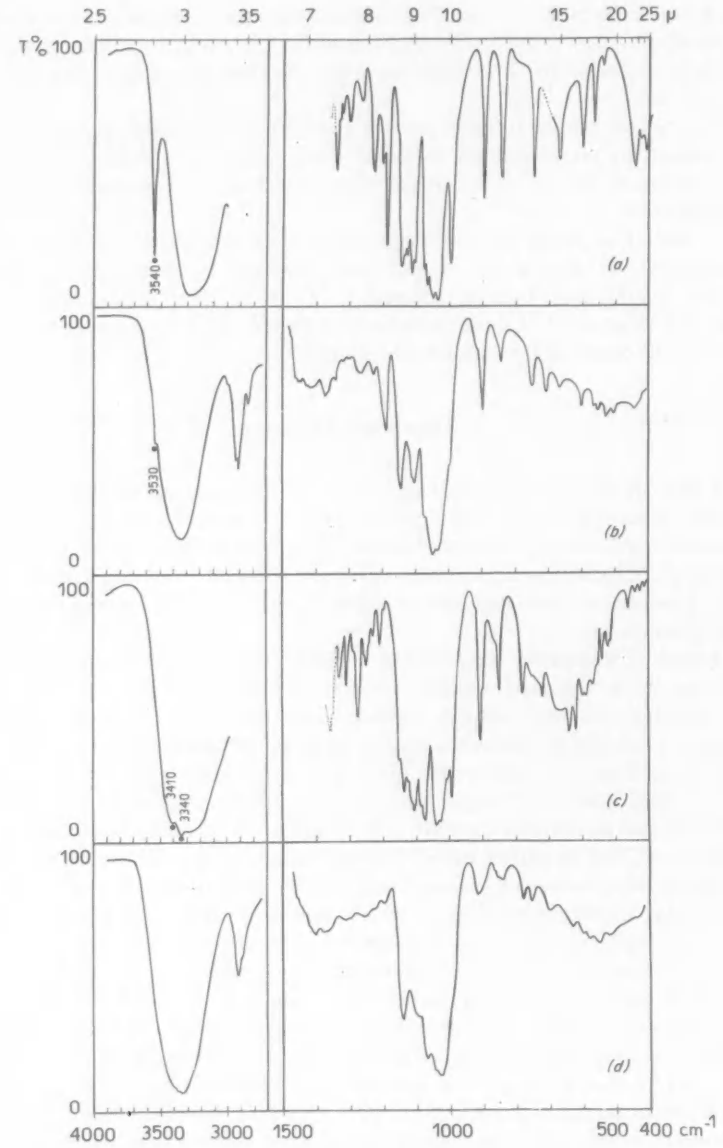

Fig. 5. Infrared spectra of deuterated α-methylglucoside, cyclodextrins, and amylose: (*a*) deuterated α-methylglucoside (nujol mull); (*b*) deuterated cyclohexaamylose (nujol mull); (*c*) deuterated cycloheptaamylose (nujol mull); (*d*) deuterated amylose film (dotted line: original amylose film).

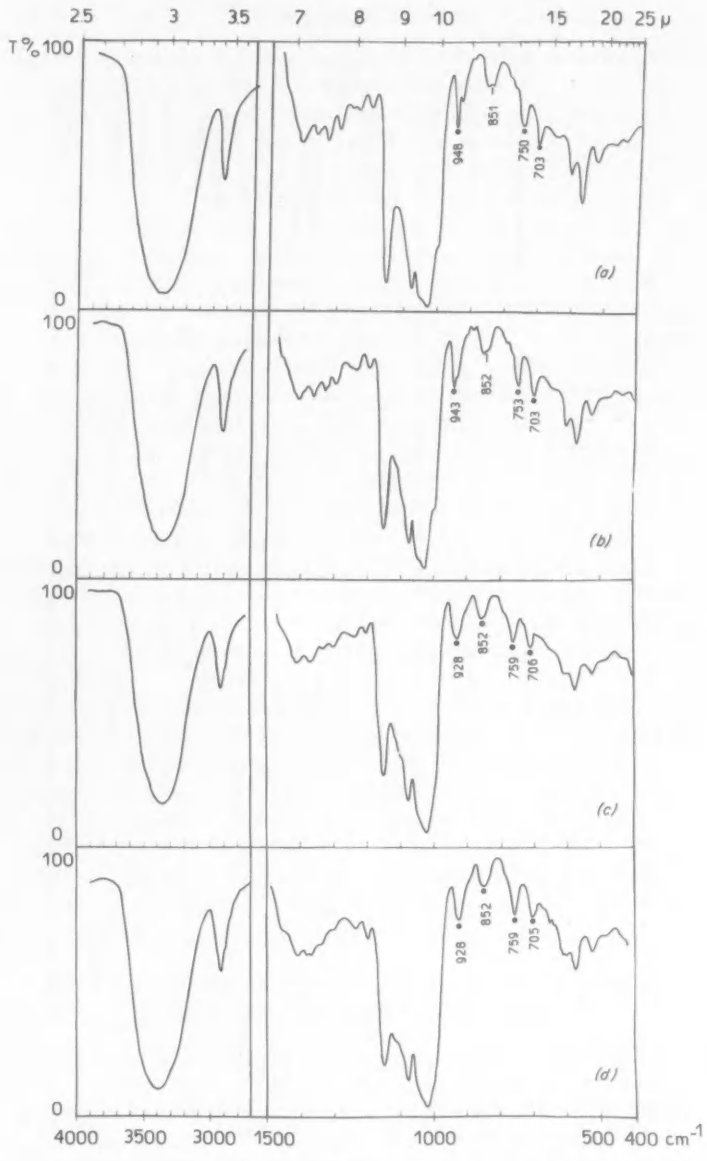

Fig. 6. Infrared spectra of amorphous (freeze dried) cyclodextrins, amylodextrin and amylose (KBr disks): (*a*) cyclohexaamylose; (*b*) cycloheptaamylose; (*c*) amylodextrin; (*d*) amylose.

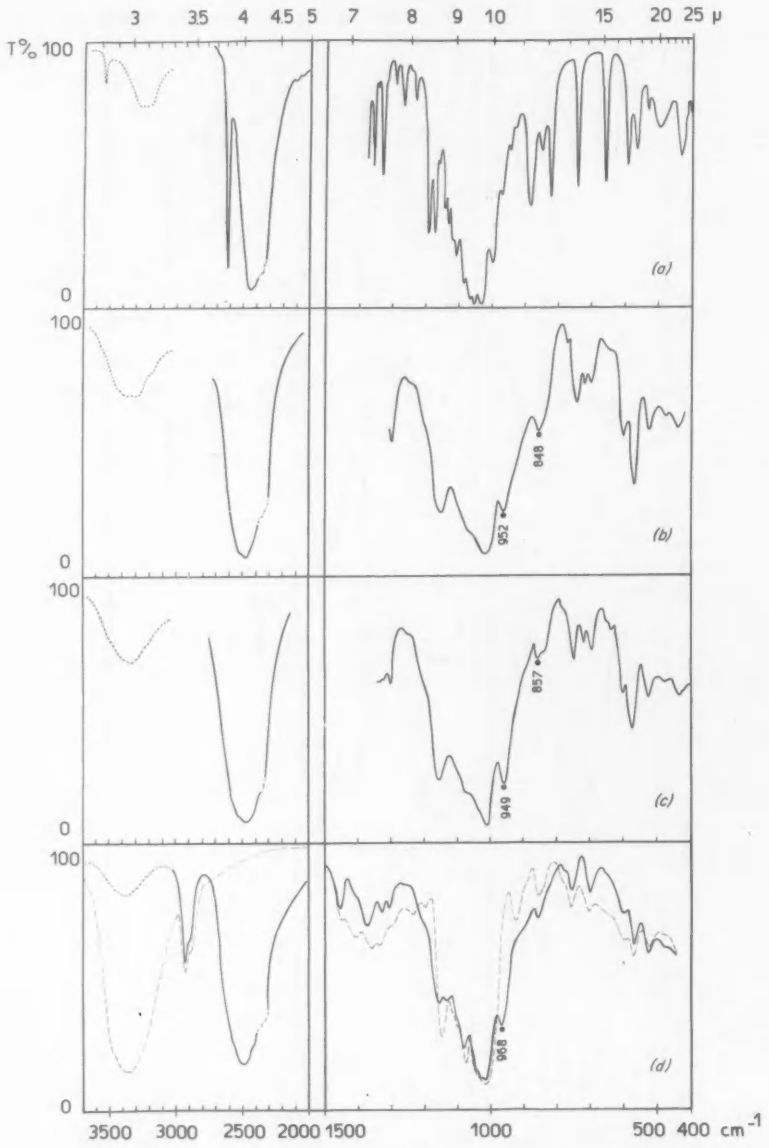

Fig. 7. Infrared spectra showing the crystallization effect of freeze drying on simple α-glucopyranosides: (*a*) crystalline α-methylglucoside (nujol mull); (*b*) freeze dried α-methylglucoside (KBr disk); (*c*) crystalline maltose (nujol mull); (*d*) freeze dried maltose (KBr disk).

3. Deuterated Products

Figure 7 shows the infrared spectra of deuterated α-methylglucoside, cyclohexaamylose, cycloheptaamylose, and amylose.

A certain contribution of nondeuterated product is still apparent in all cases. This is a common feature of infrared spectra of deuterated saccharides so far reported[5–7,11] and in this case it is to be considered mainly as a reflection of the equilibrium reached with water vapor under the experimental conditions used. Actually, we obtained occasionally in the 3200–3500 cm.$^{-1}$ region some spectra of amylose film free of residual O—H absorption. It is to be pointed out that "residual" O—H bands in the spectrum of deuterated amylose film do not display the fine structure pattern which would have implied the presence in amylose of some nonaccessible crystalline regions like those of cellulose.[15] This is in agreement with the findings of Taylor and co-workers[16] that hydroxyl hydrogens in amyloses and starches are fully exchangeable with deuterium.

An infrared spectrum with well-defined peaks is shown by deuterated α-methylglucose. O—D bands in the 2300–2600 cm.$^{-1}$ region, including the sharp peak at 2615 cm.$^{-1}$, closely reproduce the O—H bands pattern of the nondeuterated product. It is therefore to be inferred that deuterated methylglucoside crystallizes in the same form as the original product.

Deuterated cyclodextrins display instead ill-defined spectra. We believe that this is due essentially to a significant absorption of atmospheric water vapor during infrared sampling and to the occurrence of more than one crystalline form.

Deuteration of amylose film affords in its infrared spectrum changes of the kind which have been observed for cellulose.[5–7,15] The general absorption level is decreased in the 1600–1100 cm.$^{-1}$ region as the result of removing O—H deformation bands, and it increases in the 1000–700 cm.$^{-1}$ region where the O—D deformation bands occur. Several bands of amylose appear not to be particularly affected by deuteration. This is the case of C—H bands in the 2900-cm.$^{-1}$ region, of the C—O bands in the 1000–1050 cm.$^{-1}$ region, and most bands at frequencies lower than 900 cm.$^{-1}$, including the C_1 group band around 850 cm.$^{-1}$.

4. Band Assignments and Comparison of Infrared Frequencies of Cyclodextrins, Amylodextrin, and Amylose

On the basis of previous data on similar or related products[5,6,8] and their behavior towards deuteration, infrared frequencies of cyclohexaamylose, cycloheptaamylose, amylodextrin, and amylose in the 1500–400 cm.$^{-1}$ range have been tentatively assigned. They are reported in Table I for "amorphous" (i.e., freeze-dried) products, since all bands other than those displayed in the amorphous state may be considered as crystalline bands.

Two "new" assignments have been made for the band around 1150 cm.$^{-1}$ and the group of three bands at about 605, 575, and 527 cm.$^{-1}$.

The 1150 cm.$^{-1}$ band which is common to most saccharides and whose

TABLE I
Infrared Frequencies of Amorphous (Freeze-Dried) Cyclohexaamylose, Cycloheptaamylose, Amylodextrin, and Amylose in the 1500–400 cm.$^{-1}$ Range

Frequency, cm.$^{-1}$				
Cyclohexaamylose	Cycloheptaamylose	Amylodextrin	Amylose	Tentative assignment
1445	1445	1450	1450	CH_2 bending
1405	1408	1410	1409	O—H in-plane bending
1363	1364	1370	1368	C—H bending
1330	1329	1330	1335	C—H bending
1293	1297	1300	1300	C—H bending
1260	1258			O—H in-plane bending
1237	1236	1234	1234	O—H in-plane bending
1199	1199	1200	1197	O—H in-plane bending
1151	1152	1150	1148	Coupled C—O (bridge) as stretching/O—H bending
1074	1074	1076	1075	C—O stretching/C—C stretching
1028	1025	1019	1018	C—O stretching/C—C stretching
948	943	928	928	Ring vibration
934	936			Ring vibration
856	856	852	852	C_1 group vibration
842	845			C_1 group vibration
750	753	759	759	Ring breathing vibration
703	703	706	705	Ring vibration
650	650	650	650	O—H out-of-plane bending
605	605	605	605	Ring vibration
570	574	575	573	Ring vibration
527	527	525	525	Ring vibration

attribution is rather controversial[7] is affected by deuteration. In deuterated amylose film it is reduced in intensity and split into two bands compared to the original film. Splitting is also more evident in the spectrum of deuterated α-methylglucoside compared to the nondeuterated product. This behavior may well be consistent with the assignment of the single band to a coupled vibration of the nondeuterated product involving, most probably, C—O (bridge) stretching and O—H bending modes. The coupling should be destroyed in the deuterated forms.*

The group of three bands at about 605, 575, and 527 cm.$^{-1}$ are shown by all the spectra of cyclodextrins, amylodextrin, and amylose thus far examined. The above bands always appear at fairly constant frequencies. They are also shown, though well reduced in intensity, in the spectrum of maltose. Cellulose shows a different pattern in this region. Tetrahydropyran shows only a band at 564 cm.$^{-1}$.

Being unaffected by deuteration and only to a small degree by the crystal-

* A further investigation of the spectra of small linear oligomers of amylose has shown that the intensity of the 1150 cm.$^{-1}$ band clearly increases on going from the monomer (α-glucose) to the tetramer (maltotetraose). The band must be therefore related to the C—O glycosidic bridge.

line form, the 605, 575, and 527 cm.$^{-1}$ bands must not be related to O—H groups or, most probably, to C—O groups. The three bands arise most probably from ring vibrations, which generally are to be expected in the spectral region below 700 cm.$^{-1}$.[17] We plan to investigate further to learn if these bands are characteristic of α-glucopyranosides.

The comparison of the infrared bands of cyclodextrins, amylodextrin, and amylose leads to the following observations. (*1*) The frequency of most bands is nearly identical for the four products. The mean frequency of the C_1 group appears also to be practically the same in this series. (*2*) Frequency differences up to 20 cm.$^{-1}$ are displayed by the band near 940 cm.$^{-1}$ and by the band near 755 cm.$^{-1}$, both attributed to ring vibrations. The first of these bands moves from 948 to 928 cm.$^{-1}$ and the second one from 750 to 759 cm.$^{-1}$ on going from cyclohexaamylose to amylose. (The more intense band of a doublet only has been taken into consideration for the 940 cm.$^{-1}$ band of cyclodextrins.) (*3*) Amylodextrin and amylose in the amorphous state show almost identical infrared spectra.

DISCUSSION

1. The C_1 Group Band

The occurrence of the C_1 group band near 850 cm.$^{-1}$ for all the products thus far examined may not be surprising, since, as it has been observed in the introduction, a band in this region has been found in all pyranosides of the α-series and has proved to be useful in differentiating them from the β-anomers.[8]

The meaning of the constant occurrence of this band and the fact that it is seen at nearly the same frequency for amorphous cyclodextrins, amylodextrin, and amylose is worthwhile discussing in connection with the problem of the conformation of glucopyranose rings.

Since α-glucopyranosides in their most stable conformation (chair C1) have an equatorial C_1—H bond (the rest of the ring C—H bonds being axial), Barker and co-workers[8] assigned the 850 cm.$^{-1}$ band to a deformation vibration of an equatorially oriented C_1—H bond. This assignment is substantiated by the occurrence of this bond in pyranosides of different series whenever an equatorial C_1—H bond should be expected.[8] Although this band is probably due to a vibrational mode involving the whole C_1 group,[18] it seems associated with a stereochemical situation in which the C_1—H bond is equatorially oriented with respect to the plane of the ring.[1]

If we assume this to be true, cyclodextrins, amyloses, and all the starch derived products of which the infrared spectra have been thus far examined should possess pyranose rings in the chair C1 conformation. Actually, it has been seen from Figure 1 that of the three most probable conformations, only C1 displays an equatorial C_1—H bond.

Because of the observed sensitivity of the 850 cm.$^{-1}$ band to modifications of the crystalline form and of the degree of hydration, it seems really im-

probable that this band should be unaffected by a conformational change of the ring and by a departure of the C_1 bond from the equatorial orientation which is known to be assumed in simple α-glucopyranosides.

Furthermore, a common conformation of glucopyranose rings in amorphous cyclodextrins, amylodextrin, and amylose is suggested by the occurrence of the C_1 group band at nearly the same frequency. This should contradict the hypothesis[1] of a B1 → 3B conformational change on going from cyclodextrins to amylose. Since only essentially linear structures can be built with 3B rings,[3] a common ring conformation in cyclodextrins and amylose would here again exclude the occurrence of rings in the 3B conformation.

2. Ring Vibrations

It is not easy to explain the shift of the frequencies of the ring vibrations on going from cyclohexaamylose to cycloheptaamylose to amylodextrin and amylose in terms of the conformation of glucopyranose rings. A change in ring vibrations may be expected either if the ring conformation changes on going from cyclic to "linear" structures ("boat" hypothesis) or if this is not the case ("chair" hypothesis). Actually, the configuration of the ring sequences and the bulkiness of the chains certainly affects ring vibrations.

This can be deduced from the results of Barker and co-workers,[8] who found a systematic movement of the above frequencies in passing from the disaccharide (maltose) through the oligosaccharides to the polysaccharides in the starch series.

CONCLUSIONS

From a general survey of the infrared data thus far available, the following conclusions can be drawn.

The behavior of the C_1 group band in all the starch derivatives thus far examined suggests a common shape of the glucopyranose rings, most probably the chair C1. At least, this should apply to amorphous products.

Further work is needed in order to characterize the structural factors which affect ring vibrations, and to clarify the significance of their shifts on going from cyclic to linear structures.

The authors are most grateful to Prof. A. Dansi for this interest and suggestions for the preparation of the investigated products, and to Prof. D. French for the gift of reference samples of cyclohexaamylose, cycloheptaamylose, and amylodextrin. Preparative work of Mr. M. Psallidi was also greatly appreciated.

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A Critical Evaluation of Infrared Methods for the Determination of the E/P Ratio of Ethylene–Propylene Rubbers

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INTRODUCTION

A general method of analyzing ethylene–propylene (EP) copolymers for comonomer content is needed which is applicable to all types of copolymers: random copolymers (I),...EPEEPEPPEPEEE...; alternating copolymers (III),...EPEPEPEP..., block copolymers (II),...PEE...EEPP...PPEE...EEP...; and copolymers containing random (or alternating) segments together with blocks along the chain, i.e. mixed I or III, and II.

Random copolymers can contain odd-numbered sequences of CH_2 groups if the EP units are head-to-tail; if some head-to-head, tail-to-tail addition occurs, then even-numbered sequences of CH_2 groups will also be present (IV).

Block copolymers sometimes have crystalline polyethylene blocks and may also contain crystalline, isotactic polypropylene blocks.

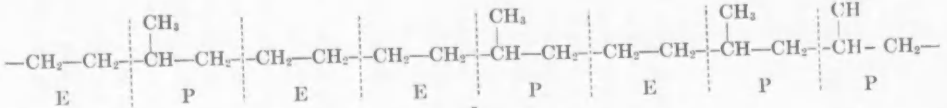
Mixed copolymers are more complex in structure than either random or block copolymers considered individually.

In view of the lack of chemical methods for assessment of copolymer type or even for the determination of the propylene content of a copolymer, the most fruitful approach so far has been in the application of infrared spectroscopy. As CH_2 groups in the copolymers can appear in many different environments, the method of analysis should be primarily concerned with the assay of CH_3 groups. Even if appreciable head-to-head, tail-to-tail addition occurs, these methyl groups are separated by two carbon atoms, and little interaction should occur. Consideration has also been given to the measurement of ethylene content or total thickness in order to complete the basis for the calculation of the E/P ratio.

METHODS OF CALIBRATION

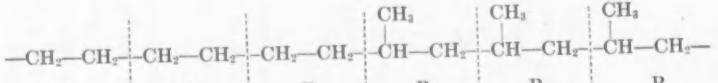
Several methods of calibrating an analytical method for the various types of copolymers exist: (*1*) use of physical mixtures of the homopolymers, i.e., polyethylene and polypropylene, in known ratios; (*2*) estimation by radioactivity counting of the polyethylene content of copolymers prepared

Random:



I.

Block:



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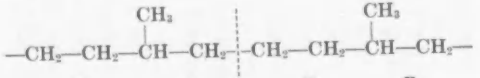
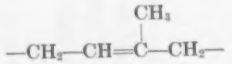
Alternating

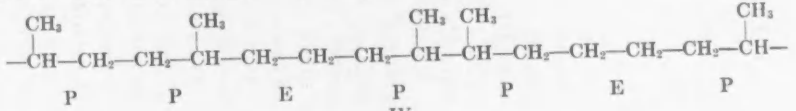


III

1,4-Polyisoprene



Containing head-to-head and tail-to-tail propylene units:



IV

from ethylene containing radioactive C^{14}; (*3*) use of a fully hydrogenated natural rubber (or *cis*-1,4-polyisoprene) as a standard; (*4*) by a direct determination of the methyl group in carbon tetrachloride solution, both atactic polypropylene and hydrogenated natural rubber being used as standards.

The use of mixtures of homopolymers in method (*1*) is applicable to the analysis of block rather than random copolymers. Method (*2*) involving radioactive tagged copolymers will be applicable to the type of structure they possess, depending on the method used for the copolymerization. Method (*3*) involving hydrogenated natural rubber applies to alternating copolymers, since hydrogenated natural rubber is an EPEP copolymer. Method (*4*) which utilizes the measurement of the methyl group in solution, can also be used in relation to any type of copolymer, provided that it is soluble; it will generally be suited to the examination of random type copolymers with an ethylene content not over 70%.

The copolymers made from C^{14}-tagged ethylene enable an independent and reliable assessment of the E/P ratio to be made, related to the C^{14} count of polyethylene itself. The one dubious point about these, however, is the possibility of some chain branching of the ethylene to give side methyl groups in the low pressure system. This will be seen from ethylene alone polymerized under the same conditions. These copolymers can be used to calibrate the spectroscopic method, which may then be used to set up secondary standards.

The spectra of polypropylene and hydrogenated natural rubber used in conjunction can also be used to produce a theoretical calibration curve, since hydrogenated natural rubber is in effect a 50 molar % propylene copolymer, and an independent standard. The absorptions at 7.25 μ and 6.85 μ for methyl and methylene, respectively, give a ratio related to the propylene content of the polymer.

The direct determination of the methyl content by utilizing the 7.25 μ absorption (due to a symmetric deformation of CH_3 groups) in carbon tetrachloride solution, was shown by Natta et al.[1] to correlate well with the ethylene content by C^{14} count. The 7.25 μ peak was also shown by Gössl[2] to be

TABLE I
Comparison of C^{14} Count with CH_3 Content of CCl_4 Solution

Sample		Polypropylene, mole-%	
		By C^{14} count	By CH_3 measurement in solution
C^{14}-labeled copolymer	1	69	67
" "	2	58.5	57
" "	3	80	80
" "	4	30	33
" "	5	50	53, 51

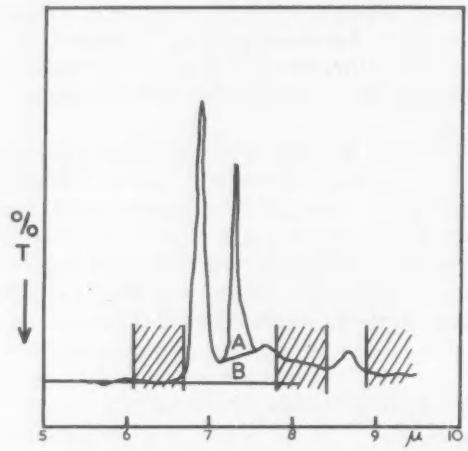


Fig. 1. Infrared spectrum of an ethylene–propylene copolymer in CCl_4 solution.

TABLE II
Molar Propylene Content by 7.25 μ Absorption in CCl_4

Sample no.	Propylene content, mole-%, by alternative baselines: Line from 5–6 μ	Line across base of peak	Difference, %
C^{14} 1	67	68	+1
" 2	57	57.7	+0.7
" 3	53, 51	51, 51	−2, +0.6
" 4	80	78	−2
" 5	54	55	+0.7, +0.4, −0.2
" 6	33	32, 30	−0.7, −0.7, −1.5, −3
" 7	38	35.5	0, −3, −2, −2.5
" 8	45, 47	44, 47.3	−1, +0.3
" 9	74	74.5	+0.5
" 10	56	56.7	0, +0.7, +0.7
" 11	62	63	+1
" 12	86	89.5	+3.5, +3.5
" 13	34	32	−2
" 14	57	56	−1
" 15	34	31	−3
" 16	35	32	−3
" 17	54	53.5	−0.5
" 18	34	34	0
" 19	54	52	−2
" 20	48	46	−2
" 21	53	51	−2
" 22	46	43	−3
" 23	39	37	−2

proportional to concentration when measured on polypropylene itself. This method is widely used for calibration purposes. It was reassessed in this laboratory for its reproducibility and accuracy under our working conditions, first by a direct comparison of polypropylene and hydrogenated natural rubber, then by checking against C^{14} count for a number of radioactive copolymers. The polypropylene and hydrogenated natural rubber gave absorptions strictly proportional to their respective methyl contents, and Table I shows the results with C^{14}-tagged copolymers.

There is a maximum divergence of 3% between the figures obtained by the two methods, 1% of which may be borne by the C^{14} count.

This method is also used by Ciampelli and Bucci,[3] except that they use baseline *A*, whereas we use baseline *B* (Fig. 1).

We have recalculated our results for polypropylene and hydrogenated natural rubber using their baseline, and find that the results are still self-consistent between the two standards. Recalculation of the propylene content of the copolymers examined however, often indicates a difference between results of the order of 2%. Table II shows the comparative figures calculated from the two alternative baselines. This gives rise to a difference of up to 3% either way over the whole range from about 40% to 80% in propylene content, and a difference of 1% between the means. For copolymers of similar structure, the variation is less, of the order of $\pm 1\%$.

The exact position of the true baseline is not known, and depends on factors such as refractive index changes near the absorptions, and overlapping of absorptions, as well as the balance of the instrument. This difference is consequently not resolvable, and there is thus some uncertainty in the true results by this standard method.

A method for the ethylene/propylene analysis which is to be of general application should give results which agree when calibrated in each of the ways mentioned.

SURVEY OF AVAILABLE ABSORPTIONS

For all such methods, careful choice of a methyl group absorption in the infrared spectra of polymers must be made. Figure 2 shows the infrared spectrum for polyethylene in its crystalline and molten states and also spectra for isotactic and atactic (or molten isotactic) polypropylene, and Fig. 3 shows the spectrum of a crystalline copolymer at room temperature and at 120°C.

The absorption band at 7.25 μ (1380 cm.$^{-1}$) due to a symmetric deformation of CH_3 groups, used by Natta et al.[1] by Kelly et al.,[4] by Ciampelli et al.,[3] and noted by Corish,[5] is an obvious candidate. Weaker bands at 8.65 μ (1156 cm.$^{-1}$) used by Gössl[2] and by Smith, Stoffer, and Hannan,[6] and at 10.3 μ (970 cm.$^{-1}$), used by Druschel and Iddings[7] ascribed to a CH_3 rocking mode and a skeletal stretching vibration respectively, may also be regarded as suitable methyl group absorptions.

The use of the 10.3 μ band as a methyl group absorption may, however,

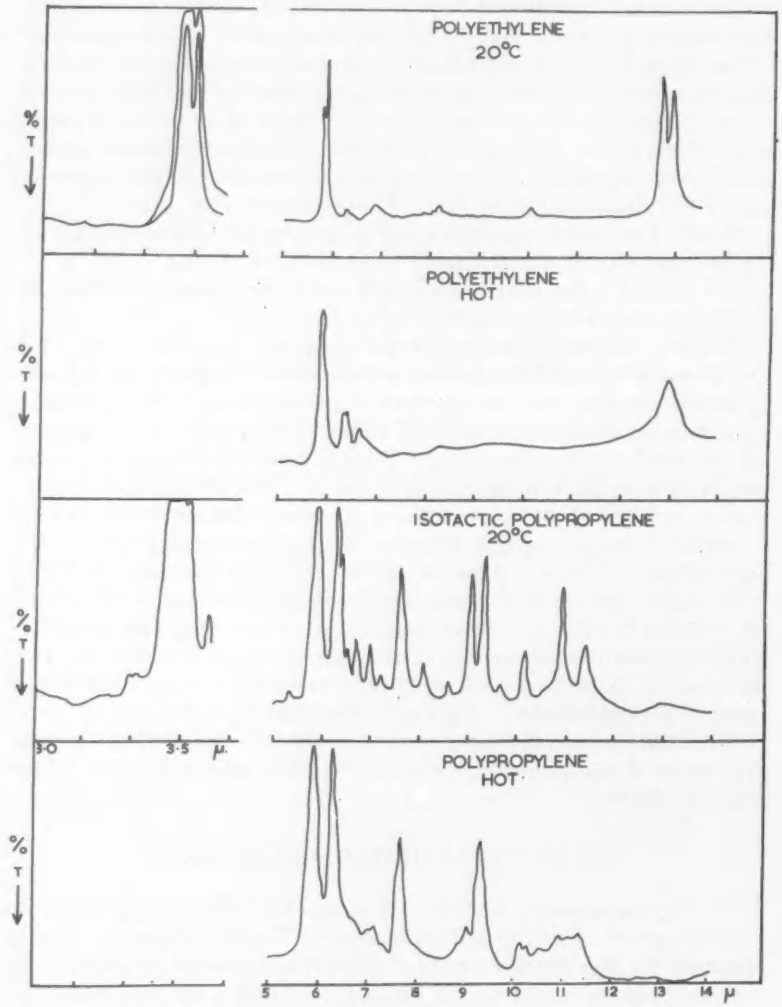


Fig. 2. Infrared spectra of polyethylenes and polypropylenes.

lead to errors due to the proximity of the *trans* RCH=CHR peak, which occurs in some copolymers containing a little unsaturation.

The CH stretching vibrations in the 3.38–3.5 μ region are obviously connected with the methyl and methylene content, but it can be seen from the spectra of polypropylene, hydrogenated natural rubber, and a 50/50 molar copolymer (Fig. 4) that the connection between the methyl content and the peak intensities is complex. Finer resolution does not reduce the complexity, and this region was therefore not studied further.

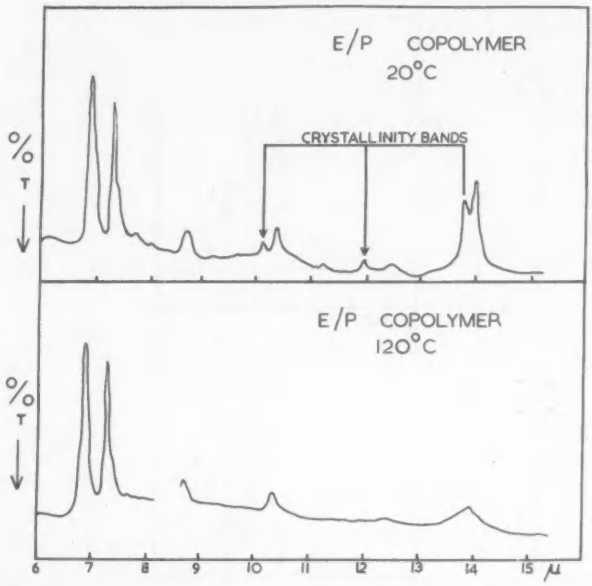


Fig. 3. Infrared spectra of an ethylene–propylene copolymer at 20°C. and 120°C

The 3.42 μ absorption has been used by Ciampelli et al.[3] and has given a calibration curve of good accuracy in their hands.

For a measure of ethylene content, or a thickness measurement, again several alternatives are available. The absorption at 6.85 μ (1460 cm.$^{-1}$) due to a CH_2 scissoring vibration is an obvious possibility.

The band at 13.9 μ (720 cm.$^{-1}$) due to $(CH_2)_n$ rocking vibrations, also intensifies with ethylene content. This has been used by Gössl[2] and Wei,[8] but it has been shown by van Schooten, Duck, and Berkenbosch[9] to be due to longer chains of CH_2 units, shorter chains $(CH_2)_3$ and $(CH_2)_2$ absorbing at 13.65 μ (732 cm.$^{-1}$) and 13.3 μ (751 cm.$^{-1}$), respectively. Polypropylene itself, containing only isolated CH_2 groups, has no absorption in this region.

Because of these considerations this region was not used in our investigations.

The absorption at 2.32 μ in the near-infrared region has also been put forward by Ciampelli et al.[3] and by van Schooten[10] as a possible measure of ethylene or as a total thickness measurement, being a combination band of a suitable intensity for comparison with the weaker methyl absorption at 10.3 μ (1156 cm.$^{-1}$).

DATA AND DISCUSSION

Comparison of Ratios

Having surveyed the field we now turn our attention to our own investigations. These were initially carried out on the 7.24, 8.65, 10.3, and 6.85 μ

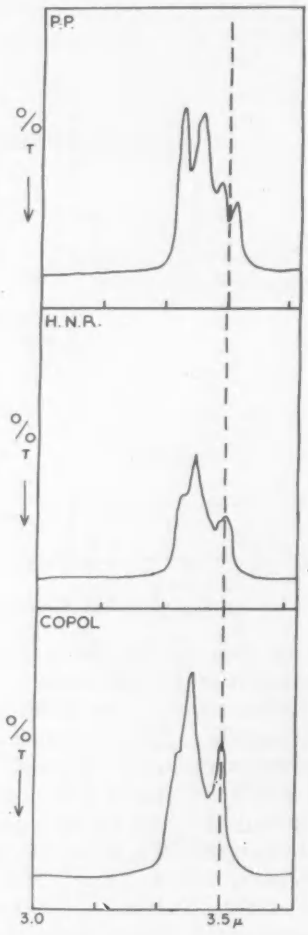


Fig. 4. Infrared spectra of polypropylene, hydrogenated natural rubber, and a 50/50 ethylene–propylene copolymer.

peaks, the absorbance ratios 7.25 μ/6.85 μ, 8.65 μ/6.85 μ, and 10.3 μ/6.85 μ being measured on mixtures of homopolymers. The infrared spectra of films of linear polyethylene and atactic polypropylene were obtained at a temperature above the melting point of the polyethylene, to minimize "state" factors. Graphs of all these ratios were drawn, and are given in Figures 5–7. Smooth calibration curves were given by all the ratios, but the 7.25 μ/6.85 μ ratio appeared the most promising. As the 8.65 μ absorption is much weaker than that at 6.85 μ, both absorbances cannot be determined very accurately on the same film. The difficulty of this differ-

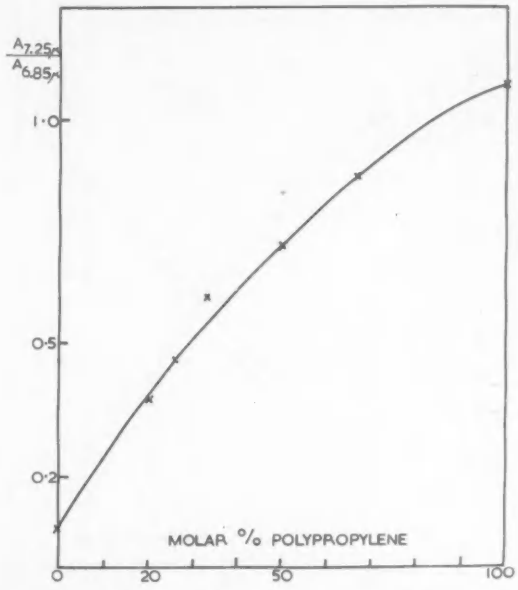


Fig. 5. Variation of $A_{7.25\mu}/A_{6.85\mu}$ with propylene content.

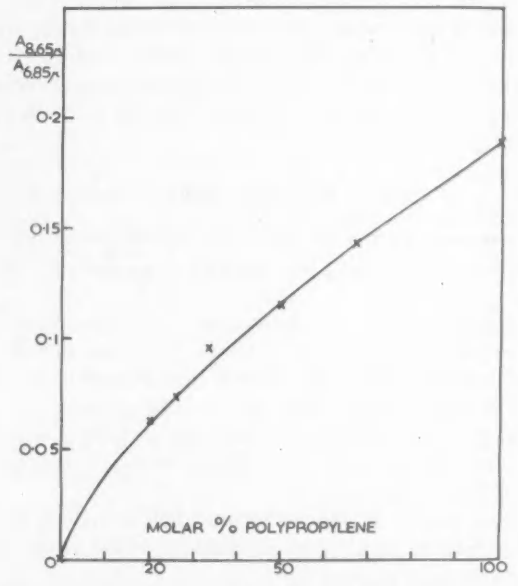


Fig. 6. Variation of $A_{8.65\mu}/A_{6.85\mu}$ with propylene content.

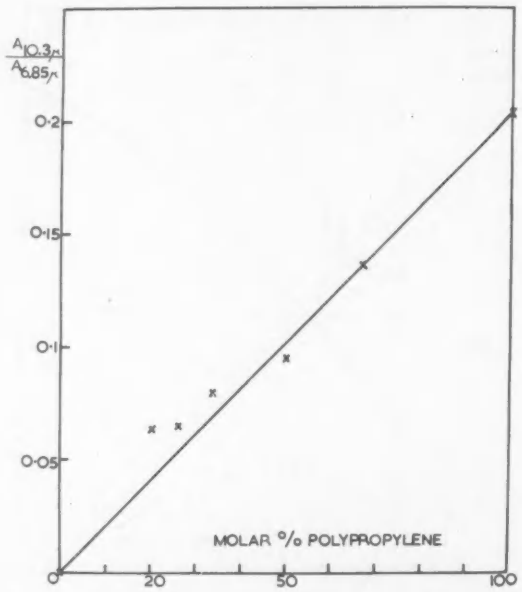


Fig. 7. Variation of $A_{10.3\mu}/A_{6.85\mu}$ with propylene content.

ence in intensities also applies to the 10.3 and 6.85 μ bands. The ratio $A_{7.25\mu}/A_{6.85\mu}$ was therefore concluded to be the best of the three for the assay of methyl groups and hence the polypropylene content of copolymers. It must be pointed out that the Marlex 50 polyethylene standard used contains a small proportion of methyl groups, thus the curve in Figure 5 does not pass through zero.

$A_{7.25\mu}/A_{6.85\mu}$ Ratio

It is now necessary to find how the other calibration methods (*2–4*) compare with method (*1*) by using the graph of $A_{7.25\mu}/A_{6.85\mu}$ versus polypropylene content.

This ratio of absorbances was determined in the same way for a range of C^{14}-tagged copolymers, the composition of which had already been determined by radioactive count. The results were plotted to give a calibration curve which proved identical with that already obtained from mixtures of homopolymers. These copolymers showed a complex absorption between 13 and 14 μ, indicating, as has been shown by van Schooten et al.[9] some $(CH_2)_2$ and $(CH_2)_3$ structures.

Fully hydrogenated natural rubber and polypropylene were next used for the determination, and the values obtained added to the existing curve. These two also fell on the curve.

From these last two results, a theoretical calibration curve was con-

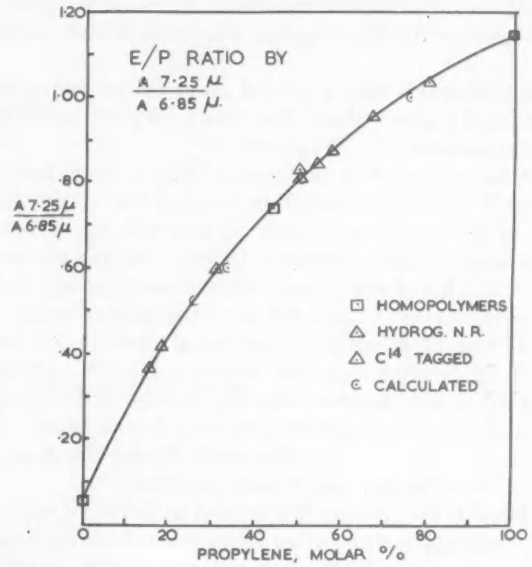


Fig. 8. Calibration curve for propylene content by $A_{7.25\mu}/A_{6.85\mu}$.

structed. For fully hydrogenated natural rubber the absorption at 6.85 μ was split up into a component given by polypropylene, the other being equated with one molar proportion of polyethylene. For a copolymer with proportions other than 50/50 molar, the 6.85 μ absorption can be calculated with respect to the methyl absorption for the polypropylene part, and the polyethylene part can be calculated and added to it. Thus the theoretical ratio can be obtained as follows.

Relative absorbances at 6.85 μ and 7.25 μ, respectively, are 1.00 and 1.14 for polypropylene; 1.00 and 0.81 for hydrogenated natural rubber; 1.00 and 0.05 for polyethylene.

For HNR the 7.25 μ absorption is split up into 0.05, the ethylene part, the remainder 0.76 being the propylene part. The value at 6.85 μ for the propylene part is then 0.699 leaving 0.301 due to the ethylene part, whence

$$A_{\text{Eth.}}/A_{\text{Prop.}} = 0.301/0.699 = 0.430$$

For 33.3% molar propylene copolymer, the values for $A_{6.85\mu}$ and $A_{7.25\mu}$ respectively, are for 2E, $0.430 \times 2 + 0.05$; for 1P, $1.00 + 1.09$; and the totals are 1.86 and 1.14. Hence,

$$A_{7.25\mu}/A_{6.85\mu} = 0.61$$

The accuracy of these calculations is governed by the "blank" given by linear polyethylene. The value of 0.05 for the ratio at $A_{7.25\mu}/A_{6.85\mu}$ is taken from the spectrum of a sample of linear polyethylene prepared in

these laboratories from diazomethane with the use of boron trifluoride as catalyst and is assumed to be a true blank and not derived from methyl side branches.

The theoretical points thus produced again fall on the existing experimental curve, and Figure 8 shows the curve finally obtained for this ratio i.e., calibration methods (*1*), (*2*), and (*3*).

The correlation between this method and the previously discussed methyl determination in carbon tetrachloride solution has already been shown deductively to be valid by agreement of each with the C^{14} count. This correlation was investigated directly. Determinations were made by both methods on a number of copolymers, both of commercially produced and laboratory scale samples. Table III shows the table of results by the two methods. Agreement is within experimental error in all cases, and is rather better for baseline *A* in the reference solution method. On the grounds of consistency therefore, the film method and the carbon tetrachloride method appear to be giving results which most nearly approach the presumed correct value, and this film method using the $A_{7.25\mu}/A_{6.85\mu}$ ratio thus falls into line with the absolute methyl content.

The reliability of the method can be seen in Table IV which shows the E/P ratio for various fractions of an E/P rubber, covering a narrow range of E/P ratios, where the results were expected to show a gradual rise in propylene content, while Table V shows duplicate and triplicate results on a number of copolymers.

The actual ratio measured is usually within ±0.01, which in the middle range most used gives values of ±1% of the mean, although at the extremes

TABLE III
Comparison of Propylene Content by Alternative Methods

Copolymer no.	Propylene, mole-%: By $\frac{A_{7.25\mu}}{A_{6.85\mu}}$	By CH_3 in CCl_4 solution: Baseline *A*	Baseline *B*
1	56	57	56
2	50	48	47
3	35, 36	34	32
4	40	38	
5	53, 54	54	52
6	34, 36	35	33
7	35	32	35
8	50	50	50
9	54	54	54
10	40	39	37
11	48	46	43
12	52	53	51
13	50	48	46
14	37	34	34
15	50	53	

TABLE IV
Results on a Fractionation of an Ethylene–Propylene Copolymer

Fraction no.	Propylene, mole-%
1	29
2	32
3	31
4	28
5	30
6	31
7	30
8	34
9	37
10	38
11	38
Whole polymer	31

TABLE V
$A_{7.25\mu}/A_{6.85\mu}$ for Films: Repeat Results

Copolymer no.	Propylene, mole-%
1	54,55,56
2	32,31
3	49,48,45
4	44,43
5	55,56
6	42,43
7	54,54,53,54
8	50,50
9	53,52
10	42,43
11	34,34,36,36

of the curve the accuracy is lower. The degree of accuracy is to some extent an individual matter, depending on the instrument, the setting of the scale, play on the paper, voltage stability, etc., affecting the final answer. The quality of film also comes into the result. Figure 9 shows the effect of changes in gain and resolution on the absorptions.

$A_{8.65\mu}/A_{2.32\mu}$ Ratio

Passing now to an alternative film method, the use of the 8.65 and 2.32 μ peaks requires thicker films; this might sometimes be an advantage, particularly with insoluble samples, which are difficult to obtain in the form of a thin coherent film. The ratio $A_{8.65\mu}/A_{2.32\mu}$ was accordingly investigated alongside the determination by the $A_{7.25\mu}/A_{6.85\mu}$ ratio. The same copolymer solution was used, and a thicker film was built up. Later, hot-pressed films were used.

Results were plotted against propylene content, and the majority of the copolymers gave a smooth curve. The hydrogenated natural rubber sample lies on the curve and so do the C^{14}-tagged copolymers (Fig. 10). The deviations from the curve are of the order of 3%, which has already been shown for the solution method to be ascribable to baseline uncertainties. There is therefore only very little intrinsic error associated with this film method. The points off the curve are not associated with any one type of copolymer, so it is likely that the inconsistencies are due to our technique. In some cases the scatter characteristics at the two wavelengths are so different that instrumental errors arise in measuring the absorbances.

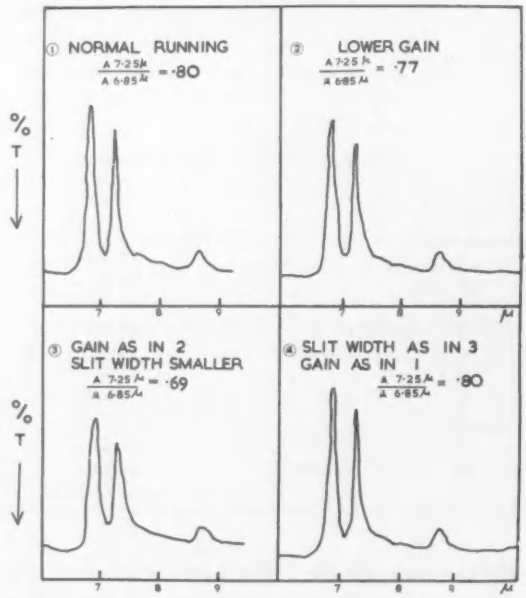


Fig. 9 Variation of $A_{7.25\mu}/A_{6.85\mu}$ with instrument setting.

We have not investigated this film method as closely as the one already described in detail. Its usefulness for insoluble copolymers is less now than formerly, as these polymers are currently only infrequently produced, and so this factor has not weighed heavily. But if interest lay in speed, this method would become more essential.

We have established for the 2.32 μ absorption that it is proportional to thickness, or total CH_2 units, within 8%. The values obtained were from 1.53 to 1.64, including polypropylene, a copolymer of high propylene content, hydrogenated natural rubber, a 50% molar copolymer, and a copolymer low in propylene.

If the 8.65 μ absorption is proportional to the number of methyl groups, then the graph of the ratio with propylene content would be a straight line, within 8%.

Unfortunately, in the two test cases of hydrogenated natural rubber and a 50/50 (w/w) mixture of homopolymers, there are special difficulties. Hydrogenated natural rubber has a small absorption at 8.3 μ, which affects the sloping baseline to the 8.65 μ absorption. The 50/50 (w/w) homopolymer mixture appears to give a higher result than that from the curve, but it is difficult to avoid separation of the components from the heated mixture.

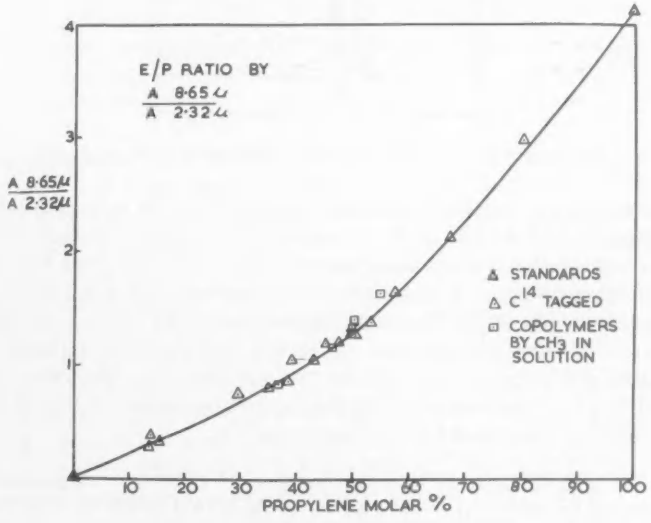


Fig. 10. Ethylene/propylene ratio by $A_{8.65\mu}/A_{2.32\mu}$.

The 8.65 μ absorption, if it is proportional to the CH_3 content of the copolymer, should bear a constant relationship to the 7.25 μ absorption. In fact, although this has not been determined with high accuracy, there is evidence of a trend in the ratio 8.65 μ/7.25 μ, from 0.14–0.15 for polypropylenes, to 0.10 for a 50% molar copolymer, and 0.05 for a 30% propylene copolymer. This may be because adjacent polypropylene units give a strictly additive effect, but the lower value given by hydrogenated natural rubber, where the CH_3 groups are also all similarly placed, points to some other cause, which appears to cancel out for all the copolymers we have analyzed.

We therefore prefer the 7.25 μ/6.85 μ absorbance ratio as being of more certain application to the general case.

EXPERIMENTAL

The experimental data for the preferred method used in our laboratory are as follows.

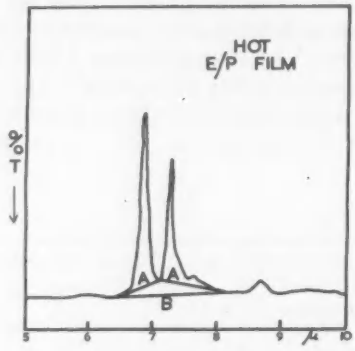


Fig. 11. Infrared spectrum showing measurement of $A_{7.25\mu}/A_{6.85\mu}$.

The polymer is dissolved in carbon tetrachloride or in xylene, decalin, or cyclohexane, and the film cast on to a potassium bromide or rock salt flat, from a hot solution if there is any precipitation in the cold, to a film thickness of about 10–20 μ. The flat is heated in a hot cell, set at ca. 120°C., and the spectrum run of the film in a molten state. The 7.25 μ and 6.85 μ peaks are measured with baseline *B* (Fig. 11), but baseline *A* normally gives the same result for the ratio of the two absorbances. The ratio is converted to propylene content using the calibration curve. A repeat run is made with the film rotated to a different position.

We wish to thank colleagues in the Chemical Research Division for the preparation of polymers and for assistance with the analysis, and the Dunlop Rubber Co. for permission to publish this paper.

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Contribution to the Study of Ethylene–Propylene Copolymers by Infrared Spectroscopy. Distribution of the Monomeric Units

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Elastomeric properties of ethylene–propylene copolymers depend not only upon the composition but also on the copolymer microstructure, i.e., on the distribution of the monomeric units along the macromolecular chain.

According to Natta et al.,[1] the best polymer should be obtained when two monomeric units are randomly alternated in the macromolecule. The random alternation of the monomers is actually only partial because somewhat longer homosequences are formed. In such a case one deals with block polymers. On the basis of some theoretical considerations on the copolymerization process[2] and also on the basis on the reactivity ratios of the two monomers, Natta et al.[1] have calculated the distribution functions of the various sequences for various catalyst systems.

Infrared spectroscopy has been widely used in connection with this problem though from different viewpoints and with different aims.[3,4]

The purpose of our work is to reanalyze the whole problem. We have focused our attention on the CH_2 rocking band in the sequence $+(CH_2)_{\overline{n}}$, where n varies from 1 to 5 or more. Some disagreement exists between the various authors[1,4–7] on the assignment of these bands, especially in the case of the $+(CH_2)_{\overline{3}}$ and $+(CH_2)_{\overline{4}}$ sequences.

We have then divided our work as follows: (*a*) assignment of the infrared bands in the spectral region between 900 and 650 cm.$^{-1}$; (*b*) calculation of the absorbances at various frequencies; (*c*) attempt at a numerical evaluation of the distribution of the monomeric units.

Assignment of the Infrared Bands in the 900–650 cm.$^{-1}$ Region

The spectra of ethylene–propylene copolymers in this frequency range show peaks or shoulders at 815, 752, 733, and 722 cm.$^{-1}$. Their intensity changes with the composition (Fig. 1).

For the assignment of these bands we have examined the spectra of several model compounds which contain the $+(CH_2)_{\overline{n}}$ sequences with different values of n. The compounds we have used are listed in Table I. In the same table we compare the results obtained in the present work with

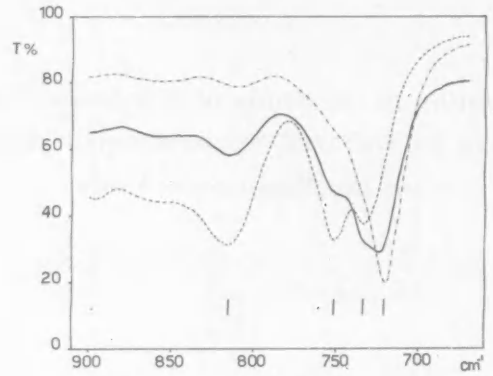


Fig. 1. Infrared spectra (900–670 cm.$^{-1}$) of ethylene–propylene copolymers at various compositions: [---- 25% (3 mol.)]; [——— 50% (3 mol.)]; [- - - - 75% (3 mol.)].

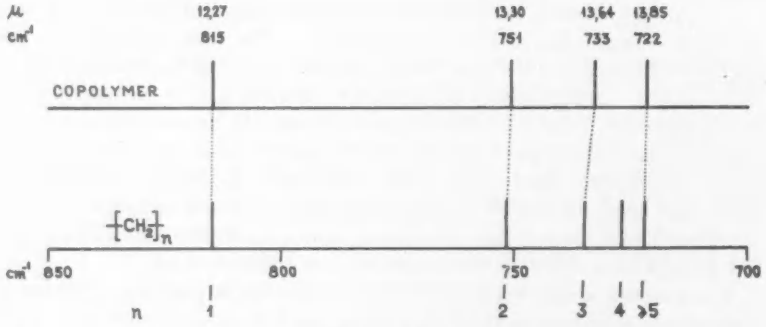


Fig. 2. Infrared spectrum (850–700 cm.$^{-1}$) of ethylene–propylene copolymers compared with the spectrum of model compounds.

those given in the literature. The results are schematically reviewed in Figure 2.

On the basis of this comparison we assign the bands at 815, 752, 733, and 722 cm.$^{-1}$ to the $\text{-}(\text{CH}_2)_n\text{-}$ sequences with $n = 1$, 2, 3, and 5 or more, respectively.

Our assignment does not agree with that proposed by van Shooten et al.[7] We think that the difference lies in the fact that those authors assigned the band at 733 cm.$^{-1}$ to the sequence $\text{-}(\text{CH}_2)_4\text{-}$. We have never been able to detect in ethylene–propylene copolymer any absorption at 726 cm.$^{-1}$ where the sequence $\text{-}(\text{CH}_2)_4\text{-}$ should occur.

We have recorded the spectrum of squalane compensated with 2,6,10,14-tetramethylpentadecane. In this case we do find a band due to $\text{-}(\text{CH}_2)_4\text{-}$ at 726 cm.$^{-1}$ (Fig. 3*D*).

TABLE I

Sequences and compounds	Frequency, cm.$^{-1}$ This work	McMurry-Thornton[6]	van Schooten et al.[7,8]	Natta et al.[9]
$+CH_2+_1$	815	785–770		
Atactic polypropylene	815			
$+CH_2+_2$	752	743–734		
2,5-Dimethylhexane			753	
Ethylene–*cis*-butene-2 copolymer	752			752
Hydrogenated poly-2,3-dimethylbutadiene			752	
$+CH_2+_3$	733–735	729–726		
2,6,10,14-Tetramethylpentadecane	735			
Squalane	735			
Hydrogenated natural rubber	735		739	
$+CH_2+_4$	726	726–724	728	
Squalane compensated with 2,6,10,14-tetramethylpentadecane	726			
$+CH_2+_5$ or more	722–721	724–722	722	
n-Heptane	722			
n-Decane	721			
n-Nonadecane	721			

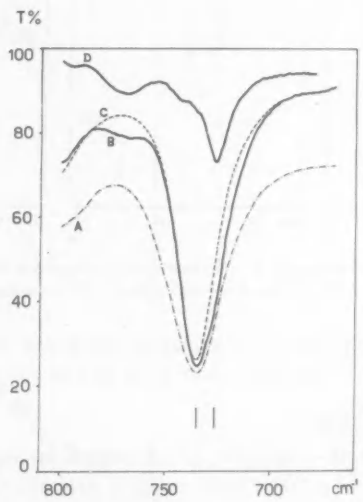


Fig. 3. Infrared spectra of model compounds: (*A*) hydrogenated natural rubber; (*B*) Squalane; (*C*) 2,6,10,14-tetramethylpentadecane; (*D*) Squalane compensated with 2,6,10,14-tetramethylpentadecane.

Absorbances at Various Frequencies

The peaks which are observed in the 800–700 cm.$^{-1}$ spectral region cannot be separated by a spectrometer owing to the large overlapping. A graphical resolution often becomes very difficult and uncertain. On the other hand, the direct reading of the peak absorbance is very unreliable because of that overlapping.

If D^{ν_i} is the absorbance determined in the spectrum of the copolymer at the frequency ν_i and D_n is the absorptivity of the bands due to various sequences we can write the following system of equations:

$$D^{752}/S = D_2 + 0.20D_3 + 0.12D_5$$

$$D^{733}/S = 0.1D_2 + D_3 + 0.35D_5$$

$$D^{722}/S = 0.50D_3 + D_5$$

In these equations S is the sample thickness.

The coefficients have been determined from the spectra of *n*-nonadecane, hydrogenated natural rubber, and atactic polypropylene (Fig. 4).

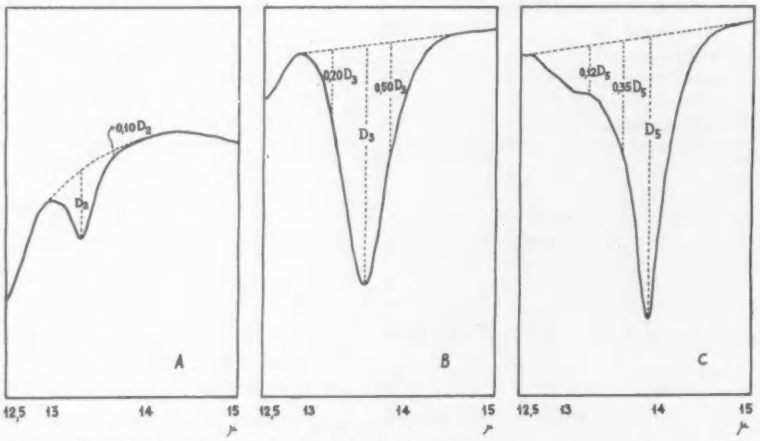


Fig. 4. Infrared absorption bands of: (*A*) atactic polypropylene with head-to-head linking; (*B*) hydrogenated natural rubber; (*C*) *n*-nonadecane.

The solution of this system of equation yields the three unknowns D_2, D_3, and D_5 which correspond to the absorbances for unit thickness* at 752, 733, and 722 cm.$^{-1}$.

We also know that $D^{815}/S = D_1$.

We have applied the method just described to many samples whose composition ranged from 20 to 100% moles of propylene. The polymeriza-

* The sample thickness is found from the 4310 cm.$^{-1}$ band by the equation $S = D^{4310}/K$, where K is the absorptivity of that frequency (for our instrument $K = 20.3$ cm.$^{-1}$).

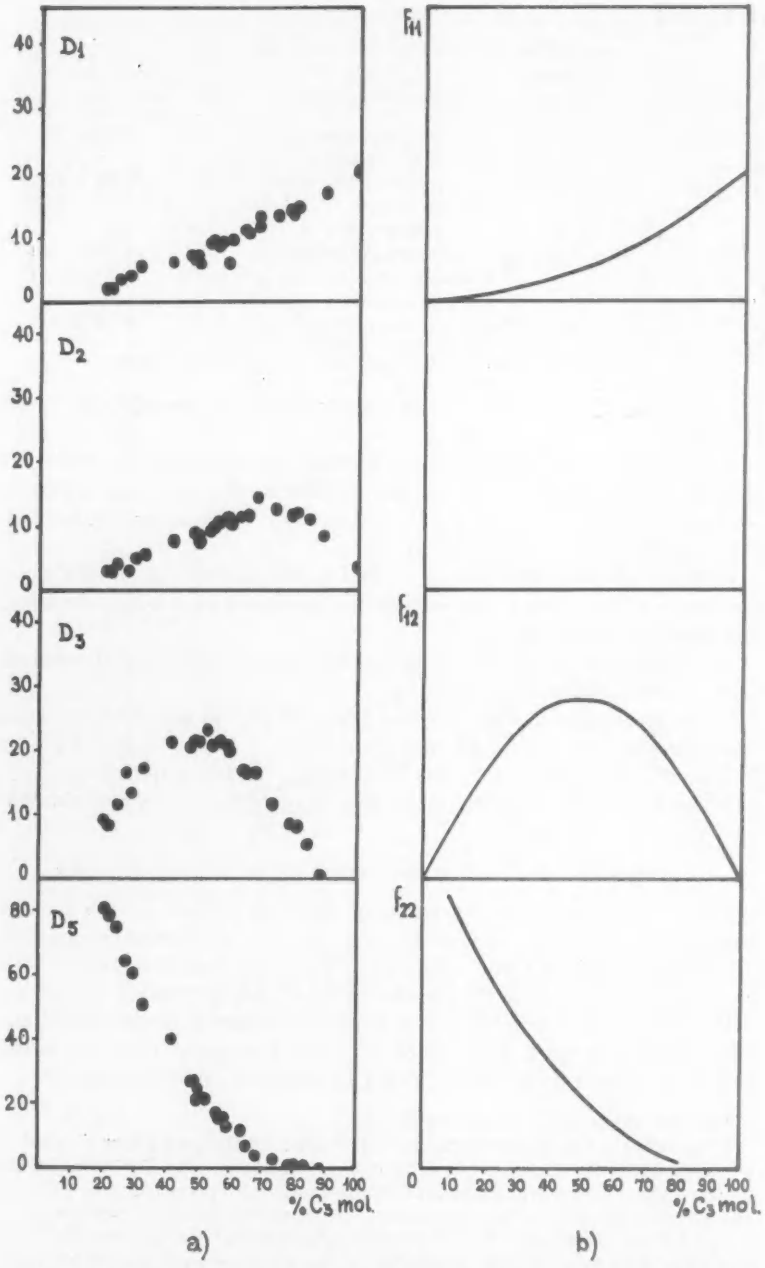


Fig. 5. Comparison between (*a*) spectroscopic experimental and (*b*) theoretical data on the distribution of monomeric units in an ethylene–propylene copolymer. (Natta et al. did not calculate the distribution of $-(-CH_2-)_2$ sequences.

TABLE II

Sequences	Absorption frequency cm.$^{-1}$	Model compounds	Absorptivities for CH_2	
			cm.$^{-1}$	mol.$^{-1}$ cm.$^{-1}$ ml.
$\text{-}(CH_2)_1\text{-}$	815	Atactic polypropylene with head-to-tail linking	0.6	0.10×10^4
$\text{-}(CH_2)_2\text{-}$	752	Atactic polypropylene with a definite amount of head-to-head linking[a]	1.0	0.15×10^4
$\text{-}(CH_2)_3\text{-}$	733	Hydrogenated natural rubber, Squalane, 2,6,10,14-tetramethylpentadecane	1.2	0.20×10^4
$\text{-}(CH_2)_{5 \text{ or more}}\text{-}$	722	Linear C_{16}–C_{19} hydrocarbons	1.2	0.25×10^4

[a] Determined from the decreasing of the intensity of the 815 cm.$^{-1}$ band.

tion has been carried out by using a special catalyst as described by Natta et al.[10]

The composition of the obtained copolymer was determined according to a procedure suggested by us previously.[11] Our results are shown in Figure 5*a*, in which the values of D_1, D_2, D_3, and D_5 absorbances are plotted against the molar composition of the copolymer.

In Figure 5*b* the values of f_{11}, f_{12}, and f_{22} are plotted against the composition.* The values of the latter set of constants have been calculated according to Natta et al.[1]

The agreement between the experimental infrared values and theoretical ones is rather satisfactory.

It can be seen from Figure 5 that the peak at 733 cm.$^{-1}$ has a maximum absorbance value for a molar composition of 50%. This fact seems to support the assignment of that band to the $\text{-}(CH_2)_3\text{-}$ sequences.

In fact only if one propylene molecule is followed by an ethylene molecule we have a $\text{-}(CH_2)_3\text{-}$ sequence.

Attempts to Calculate the Distribution of the Monomeric Units

For a quantitative determination of the CH_2 content in the various sequences it is necessary to know the absorptivities at different frequencies.

We have obtained those values from the long chain compounds with structures very similar to the ones occurring in the copolymer.†

In Table II we list in the first column the sequence, in the second the absorption frequencies, in the third the model compounds used, and in the last the K_{ν_i} absorptivities (cm.$^{-1}$) for CH_2 which we have determined.

* For the definition of f_{11}, f_{12}, f_{22} see Natta.[1]

† The values of the absorptivities for $\text{-}(CH_2)_3\text{-}$ and $\text{-}(CH_2)_5\text{-}$ sequences obtained in our work agree with those given by Thornton and McMurry. See Table II. On the contrary, values different from those given by these authors have been found for $\text{-}(CH_2)_1\text{-}$ and $\text{-}(CH_2)_2\text{-}$ sequences. This discrepancy may be understood because different model compounds have been used. The main difference is that Thornton and McMurry have used short chain hydrocarbons. Furthermore, absorption frequency used in our determinations does not coincide with that proposed by the same authors.

Using D_n and K_{ν_i} we calculated for various samples the CH_2 content (in grams/100 g.) corresponding to each band at frequency ν_i.

These results are listed in Figure 6, where the quantity G_n is defined as $G_n = D_n/K_{\nu_i}$.

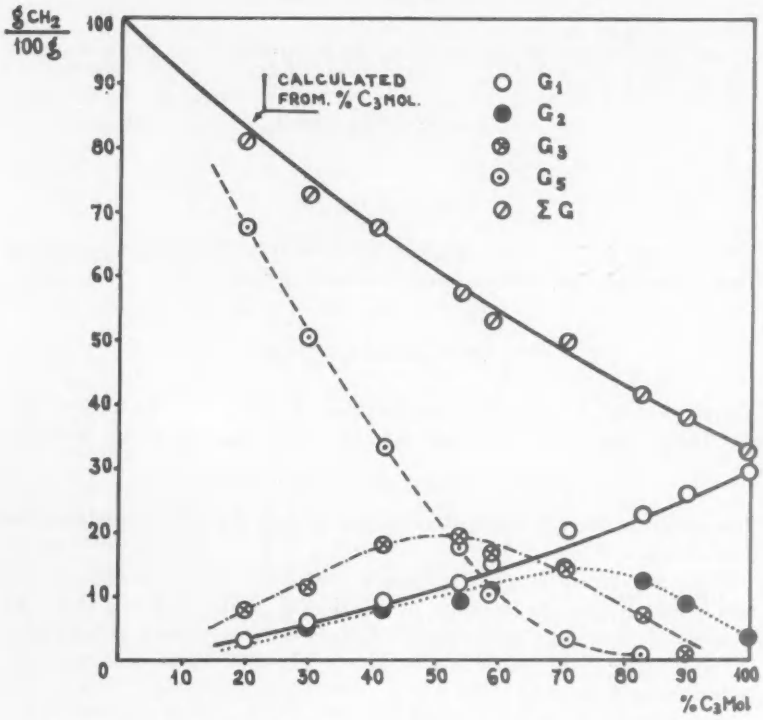
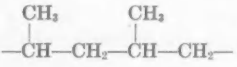


Fig. 6. Distribution of $+CH_2+_n$ sequences as a function of molar composition.

In order to get a better understanding of the structure of the copolymer we think it more useful to transform the quantity G_n into another one expressed as percentages of propylene and ethylene at the various frequencies.

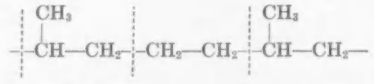
(*a*) $+CH_2+_1$ sequences can be obtained only from a head-to-tail linking of propylene:



If $G_1 = D_1/K_{815}$ (in gram CH_2/100 g.) then we must have

$$3G_1 = \%C_3^{815} \text{ (g./100 g.)}$$

(*b*) $+CH_2+_3$ can be obtained only when ethylene and propylene are regularly alternated and when propylene polymerizes with head-to-tail linking:



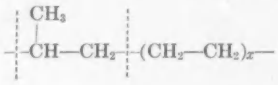
To the total weight of this sequence the contributions of propylene and ethylene are 1/3 and 2/3, respectively. Thus:

$$G_3 = \%C_3^{733} \text{ (g./100 g.)}$$

and

$$0.66\, G_3 = \%C_2^{733}$$

When $n = 2, \ldots, 5$ or more, one needs to introduce some approximations. For $n = 5$ or more we have the following chain:

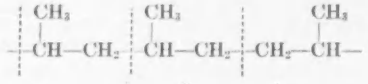


where $x = 2, 3, \ldots$, etc. If we neglect the contribution to the total weight of (CH_2) groups of the methylene adjacent to the CH_3—CH group, we have:

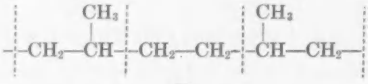
$$G_5 = D_5/K_{722} = \%C_2^{722} \text{ (g./100 g.)}$$

This approximation is reasonable when x is large (i.e., the propylene content is low).

When x is small (i.e., the propylene content is large) the error is still negligible because the content of $+(CH_3)CH—CH_2—(CH_2—CH_2+_x$ sequences is very small. The case of $+CH_2+_2$ is more difficult and we were forced to make more drastic assumptions. The $n = 2$ sequences can occur in two cases (I and II):



I



II

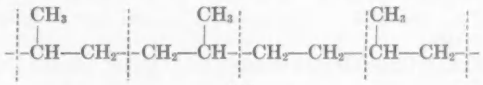
Let us assume that both I and II chains have the same probability of occurring in a copolymer chain.

If $G_2 = D_2/K_{752}$, after some consideration of the models I and II it can be seen that

$$1.5G_2 = \%C_3^{752} \text{ (g./100 g.)}$$

$$0.5G_2 = \%C_2^{752} \text{ (g./100 g.)}$$

The combination of models I and II gives rise to the structure III



III

which corresponds to a propylene content of 75 mole-%. In Figure 5*a* the maximum of the D_2 curve is at about 75%, which seems nicely to agree with our assumptions.

TABLE III
Experimental Results

		$+CH_2+_1$, 815 cm.$^{-1}$	$+CH_2+_2$, 752 cm.$^{-1}$		$+CH_2+_3$, 733 cm.$^{-1}$		$+CH_2+_3$, 722 cm.$^{-1}$	
No.	C_3, Mole-%	C_3, mole-%	C_2 mole-%	C_3, mole-%	C_2, mole-%	C_3, mole-%	C_2 mole-%	Σ
1	20.6	6.4	1.5	3.0	5.7	5.7	74.1	96.4
2	24.8	12.1	2.3	4.7	7.2	7.2	70.1	103.6
3	29.9	13.8	2.7	5.5	8.5	8.5	59.9	98.9
4	33.1	20.4	3.2	6.5	11.1	11.1	49.1	101.4
5	41.9	22.3	4.6	9.2	14.2	14.2	40.3	104.8
6	47.8	25.5	5.5	11.0	14.0	14.0	27.6	97.6
7	50.3	22.3	4.8	9.5	14.7	14.7	25.8	91.8
8	52.8	29.4	5.6	11.3	16.1	16.1	21.9	100.4
9	56.3	33.9	6.6	13.3	15.2	15.2	18.3	102.5
10	59.2	25.6	7.2	14.4	14.9	14.9	17.5	94.5
11	60.2	41.2	7.7	15.4	15.3	15.3	14.4	109.3
12	63.8	44.6	7.4	14.8	12.3	12.3	13.0	104.4
13	65.4	43.3	7.7	15.4	12.2	12.2	7.3	98.1
14	68.9	53.8	9.6	19.2	12.2	12.2	4.0	111.0
15	73.8	55.3	8.6	17.2	8.8	8.8	2.7	101.4
16	79.0	58.3	8.1	16.2	6.5	6.5	0	95.6
17	81.0	63.6	8.5	17.0	6.3	6.3	0	101.7
18	84.6	73.8	6.1	12.2	1	1	0	94.1
19	88.9	74.6	6.1	12.2	1	1	0	95.0

Finally one can go from quantities expressed as grams/100 grams to mole-per cent.

In Table III we list the molar contribution of ethylene and propylene to each band coming from the various sequences.

From the sums of the various contributions and keeping in mind the previous discussion we can conclude that our results seem to be consistent with our assumptions.

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Experimental Contribution to the Infrared Study of the Crystallinity of Polymers

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The infrared spectrum of several polymers shows absorption bands that disappear in the molten state or in solution. These bands are usually called infrared crystallinity bands, and those polymers, which show such bands, have been called crystalline.

It is our aim to collect and examine the various experimental data that may be useful in clarifying and defining the origin of the so-called "infrared crystallinity bands" in the polymers. The infrared data have been often compared with the x-ray diffraction data. On the basis of this comparison, it is possible to distinguish three main types of polymers depending on their behavior: (*1*) polymers which show infrared crystallinity bands and for which the x-ray diffraction shows the existence of a three-dimensional lattice (Most polymers behave like this; and here we cite only those examined in more detail: polyethylene,[1] polyoxymethylene,[2] *trans*-1,4-polybutadiene,[3] α-modification, *cis*-1,4-polybutadiene,[4] isotactic and syndiotactic 1,2-polybutadiene,[5,6] isotactic polypropylene,[7] isotactic *trans*-1,4-polypentadiene,[8] isotactic polystyrene,[9] various substituted polystyrenes,[10] and various mechanical polystyrene–poly-*p*-methylstyrene mixtures[10]); (*2*) polymers that show infrared crystallinity bands, but give no evidence of a three-dimensional lattice by x-ray diffraction (this is the case of the smectic or paracrystalline forms of isotactic polypropylene,[7] isotactic *trans*-1,4-polypentadiene,[8] and isotactic *trans*-1,4-polyhexadiene.[11] Such modifications are obtained by rapid cooling of the molten polymer; by annealing, they can be transformed into a modification with a behavior analogous to that shown by polymers of the first type, as revealed mainly by x-ray and by infrared studies); (*3*) polymers that do not show infrared crystallinity bands, but for which the x-ray diffraction shows the existence of crystallinity (this is the case of the β-modification of *trans*-1,4-polybutadiene[4] and of the styrene–*o*-fluorostyrene copolymers in a concentration range of 30–70% styrene).

Consequently it seems that infrared spectroscopy and x-ray diffraction studies applied to polymers may give different information on the crystallinity of the samples under examination.

Natta[10] has explained these differences by assuming that the infrared crystallinity bands are due mostly to the regularity of the polymeric chain

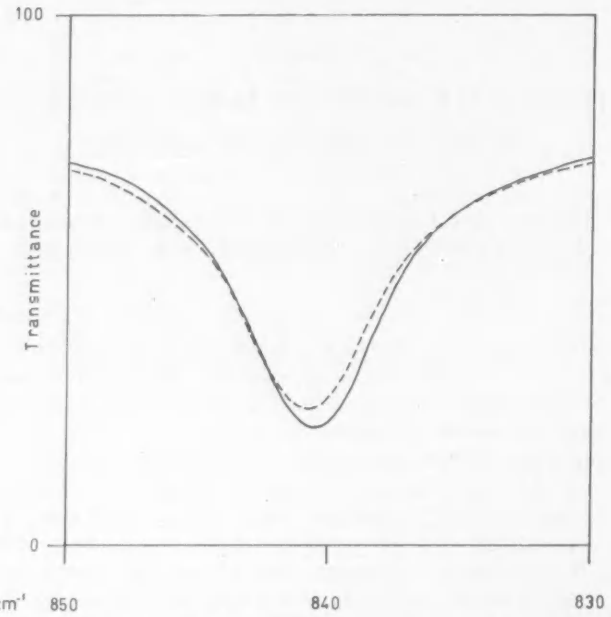

Fig. 1. Spectral differences in the 830–850 cm.$^{-1}$ region of (- - -) crystalline and (——) smectic modifications of isotactic polypropylene.

independently of the regular packing of the single chains in a three-dimensional lattice.

Only a few cases have been observed for which the infrared spectrum of a polymer cannot be explained by considering only one polymer chain and neglecting the possible interactions with other chains belonging to the same unit cell. This is the case of polyethylene, which has been widely described by several authors,[1] of the orthorhombic modification of polyoxymethylene, recently described by Zamboni et al.,[2] and probably of the α-modification[4] of *trans*-1,4-polybutadiene (stable below 60°C.) for which, unfortunately, accurate data concerning its structure have not yet been given; however, its infrared spectrum cannot be explained on the basis of a single chain.

Therefore, the influence of the crystalline lattice on the spectrum of the isolated polymeric chain has been so far shown in very few cases. By an accurate investigation, we have tried to point out this influence in several other cases which have not been previously reported. We deal mainly with polymers able to yield a smectic form.[7,8] According to Natta,[7,8] the infrared spectrum of the smectic form of a polymer can be considered that of a hypothetical isolated chain; therefore a comparison between the infrared spectra of the smectic and crystalline modifications may reveal the influence of the crystalline lattice on the single chain.

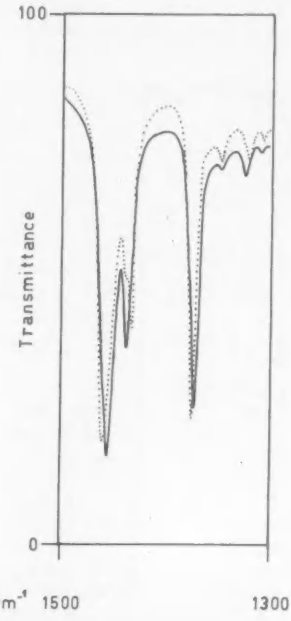

Fig. 2. Spectral differences in the 1300–1500 cm.$^{-1}$ region of (- - -) crystalline and (——) smectic modifications of isotactic *trans*-1,4-polypentadiene.

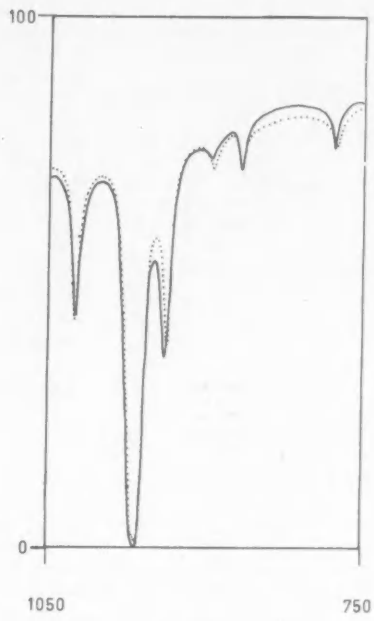

Fig. 3. Spectral differences in the 750–1050 cm. region of (- - -) crystalline and (——) smectic modifications of isotactic *trans*-1,4-polypentadiene.

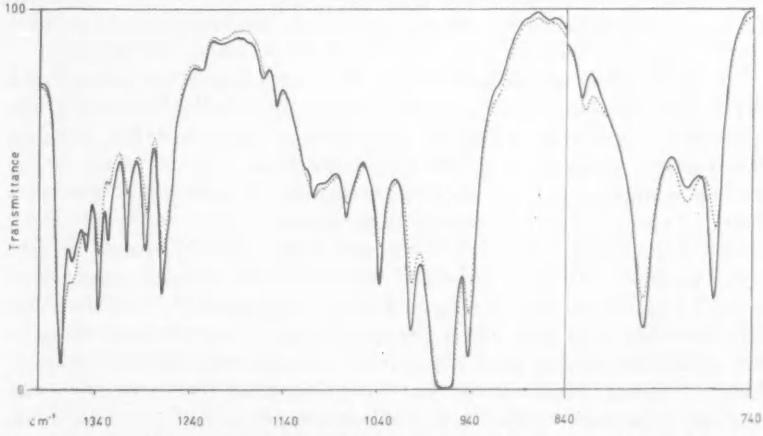

Fig. 4. Spectral differences in the 740–1400 cm.$^{-1}$ region of (- - -) crystalline and (——) smectic modifications of isotactic *trans*-1,4-polyhexadiene.

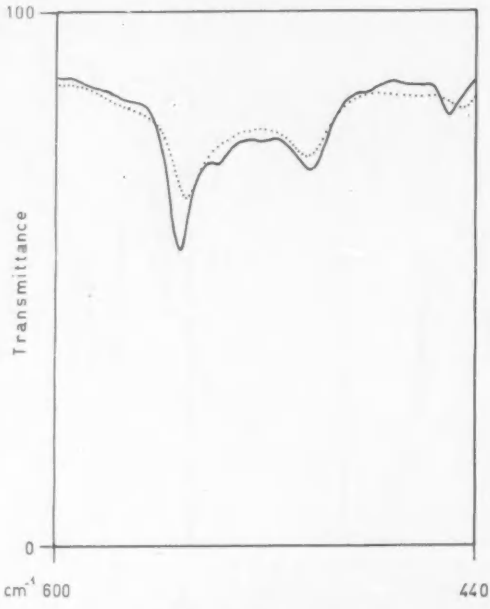

Fig. 5. Spectral differences in the 440–600 cm.$^{-1}$ region of (- - -) crystalline and (——) smectic modifications of isotactic *trans*-1,4-polyhexadiene.

We have studied the following polymers: isotactic polypropylene, isotactic *trans*-1,4 polypentadiene-1,3, isotactic *trans*-1,4-polyhexadiene-1,3. In the case of isotactic polypropylene we have observed only one difference between the infrared spectra of the smectic and of the crystalline forms: the former shows a band at 840.8 cm.$^{-1}$, the latter a band at 840.4 cm.$^{-1}$ (Fig. 1).

Much more marked differences are observed between the smectic and crystalline forms of *trans*-1,4-polypentadiene-1,3. The bands that in the smectic form occur at 772, 895.5, and 939 cm.$^{-1}$ shift to 770.5, 893, and 936.5 cm.$^{-1}$, respectively in the crystalline form (Fig. 3). Also in the carbon–hydrogen bending region, some changes are observed. The spectrum of the smectic form shows bands at 1454, 1435, and 1372 cm.$^{-1}$, which in the crystalline form shift to 1459, 1430.5, and 1374 cm.$^{-1}$ (Fig. 2).

Variations of the same order are observed in the infrared spectrum of *trans*-1,4-polyhexadiene-1,3 (Figs. 4 and 5). The bands that for the smectic form show up at 1056, 829.5, 759.6, 548.8, 504.4, and 445 cm.$^{-1}$ occur in the crystalline form at 1037, 831.5, 765.5, 552, 503, and 450 cm.$^{-1}$, respectively. A weak band at 538 cm.$^{-1}$ is observed in the spectrum of the crystalline polymer, while it is absent in the spectrum of the smectic modification.

For almost all bands, both for isotactic polypropylene and for isotactic

TABLE I
Relationship between Chain–Chain Distance in some Crystalline Polymers and Corresponding Variations in the Infrared Spectrum Due to the Packing in the Crystalline Lattice

Polymer	Probable action of crystalline lattice on infrared spectrum	Chain–chain distance, A.	Reference
Polyoxymethylene, orthorhombic form	Splitting of about 20 cm.$^{-1}$	4.0	Carazzolo[12]
Polyethylene	Splitting of about 10 cm.$^{-1}$	4.45	Natta and Corradini[13]
trans-1,4 Polybutadiene	Presence of infrared bands probably due to lattice	4.54	"
cis-1,4 Polybutadiene	No evidence (but no smectic form)	4.6	"
Isotactic *trans*-1,4-polypentadiene	Slight shifts of about 2–5 cm.$^{-1}$	5	Ciampelli[14]
Isotactic *trans*-1,4-polyhexadiene	"	5.0	Perego and Bassi[11]
Isotactic polypropylene[a]	Very slight shifts	5.3	Natta and Corradini[13]
Isotactic polystyrene[a]	No evidence (but no smectic form)	7.3	Natta et al.[15]

[a] A vicariance of up and down chains is also possible in these polymers.

trans-1,4-polypentadiene and *trans*-1,4-polyhexadiene, variations of intensity are observed between the bands of the smectic and of the crystalline modifications.

In the case of polymers that do not show the smectic modification, it is necessary to study them in isotopic dilution or in isomorphous matrices. We have not yet obtained sufficiently accurate data to permit the spectrum of the hypothetic isolated chain to be observed.

If the spectral changes previously described are really due to the influence of the crystal lattice of the polymer chain, one could try to correlate them with the degree of packing. However, most probably those spectral variations are not ascribable only to the chain–chain distance. Other factors must be taken into account. Among them an important role can be played by the possible vicariance[10] between up and down isomorphous chains in some isotactic polymers.

The intensity of such bands has been often used in order to obtain an indication on the crystallinity of the polymers. We think that intensity data require at this point some comments.

In the unusual case in which it is possible to identify and separate a band that can be surely attributed to interactions between adjacent chains, the intensity is a measure proportional to the volume of the crystalline part of the polymer sample. On the contrary, in the case of a smectic modification, the measurement gives values proportional to the number and length of regular chain segments present in the polymer.

These are extreme cases, but also intermediate ones exist. Those infrared bands, which slightly vary their position from the smectic to the crystalline can still be somehow related with the crystalline volume. Nothing can be said of those bands that are in the same position in both phases.

Thus, having pointed out the existence of various types of infrared crystallinity bands, we propose the use of the term "infrared bands of regularity of chain" for those infrared crystallinity bands which are more likely connected with the chain regularity and not with the crystalline lattice (e.g., smectic modifications), and of the term "infrared crystallinity bands" for those bands connected with the existence of interactions between chains belonging to the same unit cell (e.g., polyethylene, orthorhombic modification of polyoxymethylene).

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Infrared Spectra of Four Substituted Poly-(1,3-butadienes) Obtained from *trans*-1,4 Polymerization

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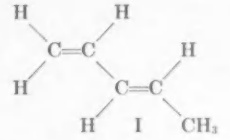
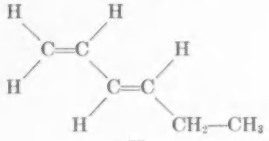
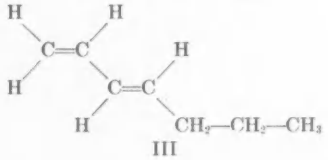
This paper reports some preliminary investigations on the infrared spectra of a homologous series of polymers obtained from 1,3-diolefins. The monomers which were polymerized are: *trans*-pentadiene-1,3 (I), *trans*-hexadiene-1,3 (II), *trans*-heptadiene-1,3 (III), and *trans*-octadiene-1,3 (IV):[1]



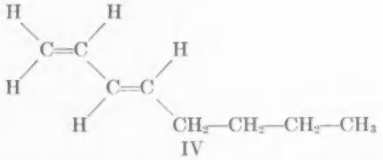
I



II

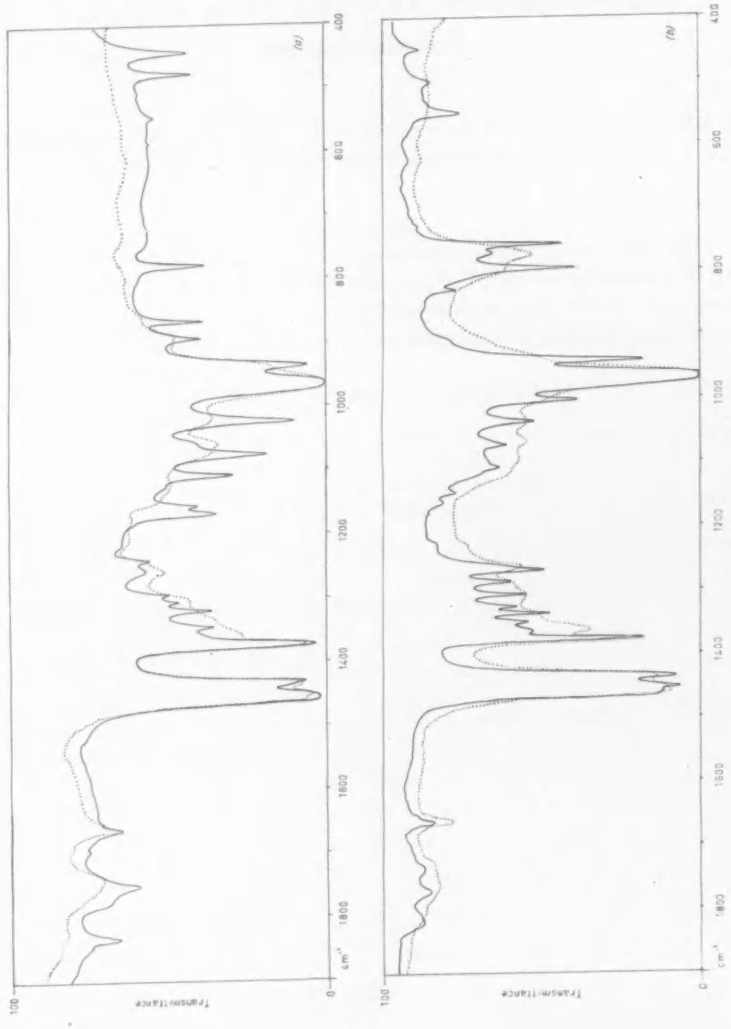


III



IV

Crystalline *trans*-1,4-polymers with an identity period parallel to the chain axis corresponding to one monomeric unit have been obtained with the use of stereospecific catalysts. The repeating unit has no elements of symmetry and therefore all its normal modes of vibrations are infrared-active:


(a)
(b)
Transmittance
100
0
400
600
800
1000
1200
1400
1600
1800
cm⁻¹

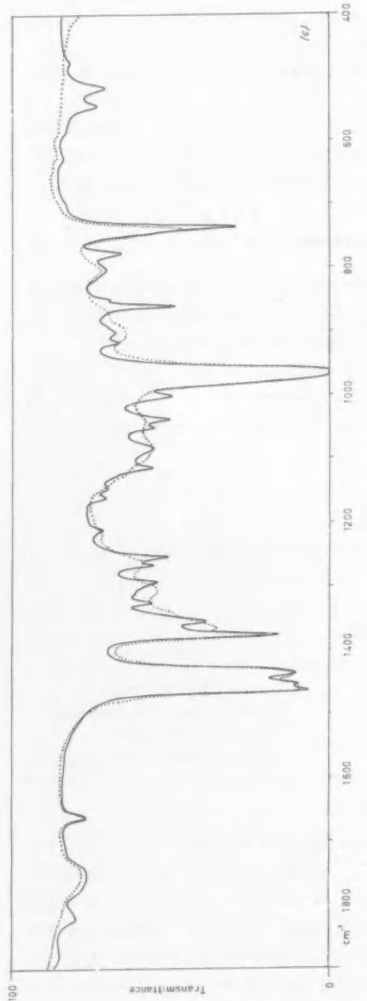
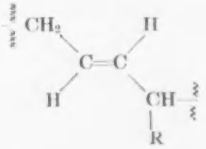


Fig. 1. Infrared spectra (——) in the crystalline state and (. . .) in the molten state of isotactic *trans*-1,4 polymers obtained from (*a*) *trans*-pentadiene-1,3; (*b*) *trans*-hexadiene-1,3; (*c*) *trans*-heptadiene-1,3; and (*d*) *trans*-octadiene-1,3 in the 1900–400 cm.$^{-1}$ region.



where R is $-CH_3$, $-CH_2-CH_3$, $-CH_2-CH_2-CH_3$, or $-CH_2-CH_2-CH_2-CH_3$.

Figure 1 shows the infrared spectra of these polymers in the range 1900–400 cm.$^{-1}$, as recorded with a Perkin-Elmer model 125 spectrophotometer. The same figure shows the spectra of the molten and crystalline polymers.

Amorphous Polymers

The spectra of the amorphous polymers (obtained in the molten state of in solution) can be easily explained on the basis of the known correlations of olefins that have been shown to be valid also for the polymers.[2,3]

The carbon–hydrogen bending vibration region is of particular interest, since it allows one to differentiate the methylenic groups of the main chain from those of the side substituent. The results obtained are reported in Table I.

TABLE I
CH_3 and CH_2 Bending Frequencies of Some Polydiolefins

Frequency, cm.$^{-1}$				
Polypentadiene	Polyhexadiene	Polyheptadiene	Polyoctadiene	Assignment
—	1460	1464	1464	Lateral CH_2 bending
1454	1455	1454	1455	Asymmetrical CH_3 bending
1435	1435	1437	1435	Chain CH_2 bending
1372	1374	1376	1376	Symmetrical CH_3 bending

Going toward lower frequencies, a strong band at 965 cm.$^{-1}$ is found for each of these polymers. That absorption can be ascribed to the carbon–hydrogen out-of-plane vibrations of the —HC=CH— group in the *trans* configuration. Next, the bands at 777, 748, and 727 cm.$^{-1}$ observed for polyhexadiene, polyheptadiene, and polyoctadiene, respectively, are assigned to the rocking vibrations of the CH_2 of the ethyl, propyl, and butyl groups, respectively.

The spectra of these polymers in the molten state or in solution can be explained mainly in terms of group vibrations alone. Only the region between 800 and 1350 cm.$^{-1}$ cannot be easily explained on that basis, since we do not have reliable correlations on the carbon–carbon vibrations occurring in this region.

Crystalline Polymers

Since the polymers belonging to this homologous series have all the same chain configuration and the same crystal structure,[4,5] we should like to find out whether it is possible to establish some correlations with the position of the so-called crystallinity bands.

The fact that some of these polymers can be obtained in a smectic form has not been taken into account in the present work. We have only compared the spectra of the molten and of the crystalline polymer obtained after several annealings.

For the four polymers, the sharpest crystallinity bands are in the spectral region ranging from 1500 to 400 cm.$^{-1}$. We did not take into account the region between 1900 and 1500 cm.$^{-1}$, where, some of the bands may be due to a slight oxidation of the samples.

In the range 1500–400 cm.$^{-1}$, the crystallinity bands for these polymers can be grouped according to the frequency ranges where they occur.

First a group of three bands occurs in the region between 440 and 550 cm.$^{-1}$; some of these bands are slightly weaker in polyheptadiene and in polyoctadiene. This is probably related to the fact that these materials have a lower degree of crystallinity than the other two polymers. Since the band at lower frequency occurs also in polybutadiene, then it can be taken as due to a normal mode mainly connected with the chain.

The second set of common features occurs in the region between 700 and 800 cm.$^{-1}$ and is due to the rocking vibrations of the CH_2 side groups. Obviously those bands do not occur in the spectrum of polypentadiene. These bands are slightly different in the case of the molten polymer. Another band is observed at about 780 cm.$^{-1}$ for all the members of the series. It splits into a doublet in the case of polyoctadiene.

The range 960–800 cm.$^{-1}$ shows no bands characteristic of the series, but only of the individual polymers.

The region between 1000 and 1250 cm.$^{-1}$ is again characteristic of the whole series, because a typical pattern is observed for all these polymers. A particular common feature is the doublet around 1150 cm.$^{-1}$.

There is a similar "zone pattern" for the whole range between 1350 and 1200 cm.$^{-1}$; in this frequency region two bands at 1345 and 1319 cm.$^{-1}$ can be observed for polypentadiene, at 1350 and 1325 cm.$^{-1}$ for polyhexadiene, at 1354 and 1325 cm.$^{-1}$ for polyheptadiene, and at 1340 and 1325 cm.$^{-1}$ for polyoctadiene.

As a tentative conclusion, we might say that from the examination of this homologous series, it seems possible that polymers of analogous chemical as well as chain structures in the crystalline state, show infrared crystallinity bands in closely similar positions. Thus, we feel that in addition to the group frequency correlations for polymers one could also obtain correlations between crystallinity bands. However, more work must be done in this direction.

We wish to thank Prof. Lido Porri, who kindly supplied the examined polymers.

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